ABSTRACT OF THESIS

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Title of Thesis Oxy-anions of Groups VA and VIA

The state of tantalum (V) in alkaline solution has been studied and the range of stability of the hexatantalate anion was found to be pH 10.8 to 13.2. At lower pH values the hexatantalate anion has been shown to condense to a colloid. Indirect evidence has been obtained, from self-diffusion studies, for the existence, in strongly alkaline solutions, of an anion, less condensed than the hexatantalate.

The products of heating mixtures of molybdenum (VI) oxide with various transition metal oxides at 640-700° C in the solid state have been investigated by X-ray diffraction. Six new molybdates of composition $Y_2O_3 \cdot 3MoO_3$, $Y_2O_3 \cdot 4MoO_3$, $HfO_2 \cdot 2MoO_3$, $V_2O_5 \cdot MoO_3$, $VO_2 \cdot MoO_3$, and $Cr_2O_3 \cdot 3MoO_3$ have been identified, these being the only compounds in these systems at this temperature. The non existence of molybdates of titanium (II), (III) and (IV), vanadium (II) and (III) and niobium (IV) and (V) has been demonstrated.

The spectral and magnetic properties of the molybdates of manganese (II), cobalt (II), nickel (II) and copper (II) indicate that the transition metal ion is octahedrally coordinated by oxygen. The spectral and magnetic properties of chromium (III) molybdate, $Cr_2(MoO_4)_3$, and vanadyl molybdate, $VO.MoO_4$, give no conclusive evidence as to the coordination of the transition metal for oxygen.

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OXY-ANIONS OF GROUPS VA AND VIA

by

George McGuire, A.H.-W.C.

Thesis presented for the Degree of Doctor of Philosophy of the University of Edinburgh in the Faculty of Science, August 1965.

Oxy-anions of Groups VA and VIA

1. The Nature of Tantalate Ion in Aqueous Solution

2. Solid Transition Metal Molybdates, Tungstates and Uranates.

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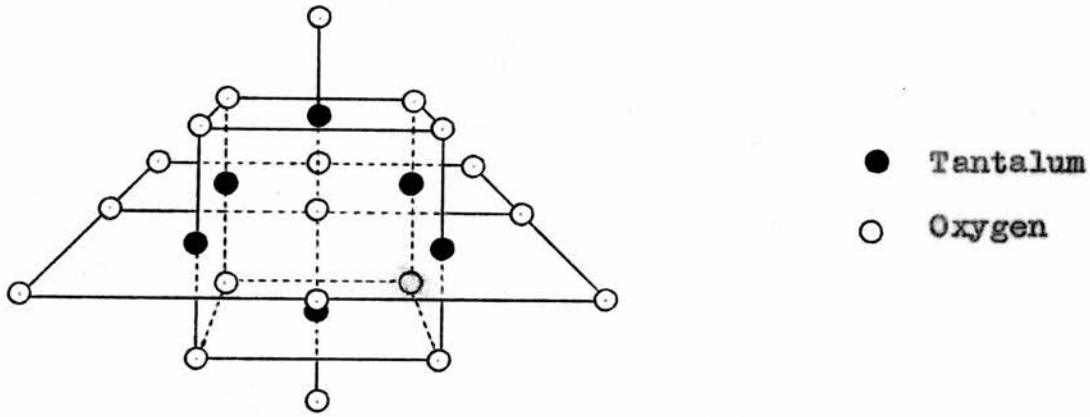
THE NATURE OF TANTALATE ION IN AQUEOUS SOLUTION

Introduction

Tantalum was first separated successfully from niobium by Marignac (1866, a), and publications prior to this are therefore unreliable. Marignac (1866, b) prepared potassium hexatantalate by fusing tantalum pentoxide with potassium hydroxide and making an aqueous solution of the melt. Analysis of the crystalline product obtained by evaporation of this solution gave the formula $4K_2O.3Ta_2O_5.16H_2O$. Using exactly the same method of preparation, Jander and Schulz (1925) formulated the product as a pentatantalate, $7K_2O.5Ta_2O_5.30H_2O$, not a hexatantalate.

In an X-ray crystallographic study of the isomorphous hydrated potassium niobates and tantalates, Halla et al. (1942) found that there were four molecules of hexaniobate and tantalate in the unit cell - 6.87 and 2.33 molecules of pentaniobate and pentatantalate respectively - which proved that the hexatantalate formulation was correct. Lindqvist and Aronsson (1954) carried out a single crystal X-ray investigation of potassium tantalate which showed the existence of the $(Ta_6O_{19})^{8-}$ anion in the crystal, the six tantalum atoms lying at the centre of octahedra, the nineteen oxygen atoms lying at the apices. No attempt was made to determine the potassium ion or water positions. Pictorially, the $(Ta_6O_{19})^{8-}$ anion, as described by Lindqvist is:-



Thus the salt formed by fusion of tantalum pentoxide and potassium hydroxide, and extraction of the melt with water, is undoubtedly the hexatantalate.

Jander (1956) published a paper in defence of his earlier work, and by extensive analysis, and optical, diffusion, cryoscopic and conductance measurements, concluded that only the heptatantalate species existed in alkaline solution and in the salts crystallised from these solutions. The results of Jander's diffusion experiments have been severely criticised by Baker and Pope (1960), and Tobias (1961) states that the salt cryoscopic method, used by Jander, has only limited value for the study of polynuclear complexes containing more than three or four metal atoms.

Although the existence of a hexatantalate in potassium tantalate crystals has been well established, only Jander and Ertel (1956) have attempted to determine the state of tantalum in solution, and their results have been shown to be of somewhat doubtful reliability. It was decided, therefore, to investigate the nature of the tantalate ion in aqueous solution by self diffusion measurements, light absorption, and potentiometric titration. During the course of this work, however, four pertinent reports have been published.

A dialysis study [Babko and Gridchina, 1963] showed that tantalum was present as polymeric compounds from normal potassium hydroxide to eleven normal hydrochloric acid solution.

Nelson and Tobias (1963) made a study of the tantalate ion in solution by spectrophotometric, e.m.f., and light scattering techniques. The position of the charge transfer band did not vary with changing tantalum or hydroxyl ion concentration in the pH range 10.8 to 12.5. The e.m.f. measurements did not indicate appreciable protonation on dissolving potassium hexatantalate in dilute potassium hydroxide solution, the number of protons bound per tantalum being constant at 0.12 in the pH range 10 to 13. Light scattering indicated a species containing six tantalum atoms within the pH range 10 to 13. These results indicate a monodisperse species containing the hexatantalate anion, $(Ta_6O_{19})^{8-}$, which has been shown to exist in potassium tantalate crystals [Lindqvist and Aronsson, 1954].

Ultracentrifugation of alkaline tantalate solutions in the pH range 10 to 13 [Nelson and Tobias, 1964] confirm previous results indicating only the hexatantalate anion.

Ultracentrifuge results by Aveston and Johnson (1964) confirm those of Nelson, and show that potassium tantalate solution, 0.008 molar in tantalum, is unstable due to precipitation at the pH of this dilution. Aveston and Johnson (1964) also obtained Raman spectra of both potassium tantalate crystals and solution. These showed a very close correspondence, which supports the conclusion that the hexatantalate anion present in the crystal is also present in solution. The structure of the hexatantalate anion as proposed by Lindqvist and Aronsson (1954) is supported by the simplicity of the Raman spectra which indicates an ion of high symmetry.

Preparation and Analysis of Potassium Tantalate Hydrate

The preparation was carried out as described by Jander (1925), except that nickel instead of silver crucibles were used, to avoid silver hydroxide precipitation. Tantalum pentoxide was added in small portions to fused potassium hydroxide and the melt was heated until clear. When cold, the product was dissolved in water, a white residue was filtered off, and the clear filtrate was evaporated in an atmosphere free from carbon dioxide. The clear, well-formed crystals obtained were washed with absolute ethanol, and kept in stoppered tubes. This was necessary as the surface of the crystals rapidly became turbid on standing in air, due to efflorescence or carbon dioxide absorption.

Tantalum was determined by precipitating tantalum pentoxide from a solution of the crystals. Decinormal hydrochloric acid was added until the solution, in a boiling water bath, became permanently acid to phenolphthalein. The precipitated tantalum pentoxide had completely coagulated after two to three hours, when it was boiled with de-ionised water, and washed with two percent ammonium nitrate solution, to remove any potassium chloride adsorbed on the surface. The precipitate, after filtration, was ignited to red heat in a silica crucible and weighed as tantalum pentoxide.

Potassium was determined by an E.E.L. flame photometer using various concentrations of potassium chloride and bromide as standards. The potassium oxide content was determined at

various dilutions, both on solutions of the crystals, and on the filtrate and washings from the tantalum pentoxide precipitation.

The potassium oxide content of the crystals was checked by titrating potentiometrically the excess of acid used in the precipitation of tantalum pentoxide. The percentage potassium oxide by this method was found to be 18.76.

	Found	Required for	
		$4K_2O.3Ta_2O_5.16H_2O$	$7K_2O.5Ta_2O_5.24H_2O$
$\%Ta_2O_5$	66.66 ± 0.22	66.59	66.92
$\%K_2O$	18.76 ± 0.08 (filtrate) 18.53 ± 0.01 (solution)	18.93	19.98

This analysis compares well with the formulation $4K_2O.3Ta_2O_5.16H_2O$ but the percentage potassium oxide found is too low to give agreement with the formulation $7K_2O.5Ta_2O_5.24H_2O$.

Diffusion

The method used was the open-end capillary method of Anderson and Saddington (1949) in which two solutions are prepared. One of them is labelled with radioactive tracer atoms, but they are otherwise identical. The labelled solution, in a capillary cell open at one end to the inactive bath solution, is kept at constant temperature for a known length of time. The cell contents are removed and the concentration of the active solution is found by counting.

By comparing this concentration with that of the active solution initially present in the cell, the self diffusion coefficient, D, can be calculated from the integrated form of Fick's Law [Anderson and Saddington, 1949; Wang, 1951],

$$\gamma = \frac{8}{\pi^2}\left(e^{-\theta} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \cdots\right)$$

where $\theta = \frac{\pi^2 Dt}{4l^2}$, l = cell length in cm., t = time in seconds and γ = ratio of final to initial counts.

If θ is large, then the series is rapidly convergent and the second and subsequent terms can be neglected. The simple expression, $\gamma = \frac{8e^{-\theta}}{\pi^2}$ can then be used which on rearrangement gives

$$D = \frac{2.303 \times 4l^2}{\pi^2 t} \log_{10} \frac{8}{\pi^2 \gamma}.$$

The assumption is made that the two isotopes behave in exactly the same way although their masses are slightly different. The cell contents and standards are counted at the same time so that no correction has to be made for radioactive decay.

The apparatus is shown in figure I. The diffusion cells were prepared from 2 cm. lengths of precision bore capillary tubing of internal diameter 0.08 cm. One end was ground flat, and the other into the shape of a cone (figure II) to reduce turbulence and eddy current formation, which might have led to loss of radioactive solution from the cell on its immersion in the bath solution. By using this shape of cell, Mills and Kennedy (1953) found that

Figure I.

Diffusion Apparatus.

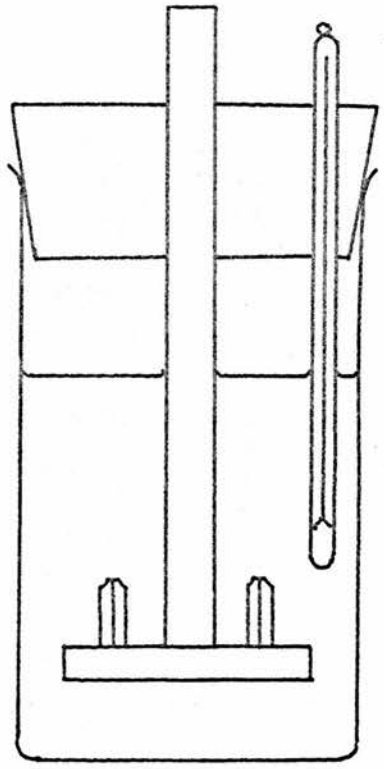


Figure II.

Capillary Cell.

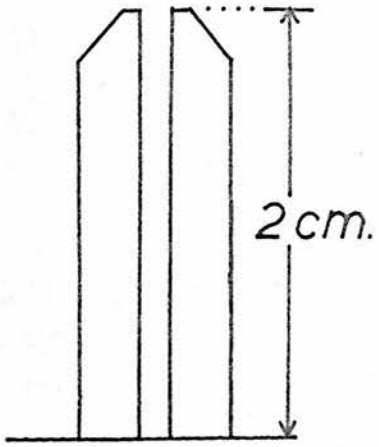
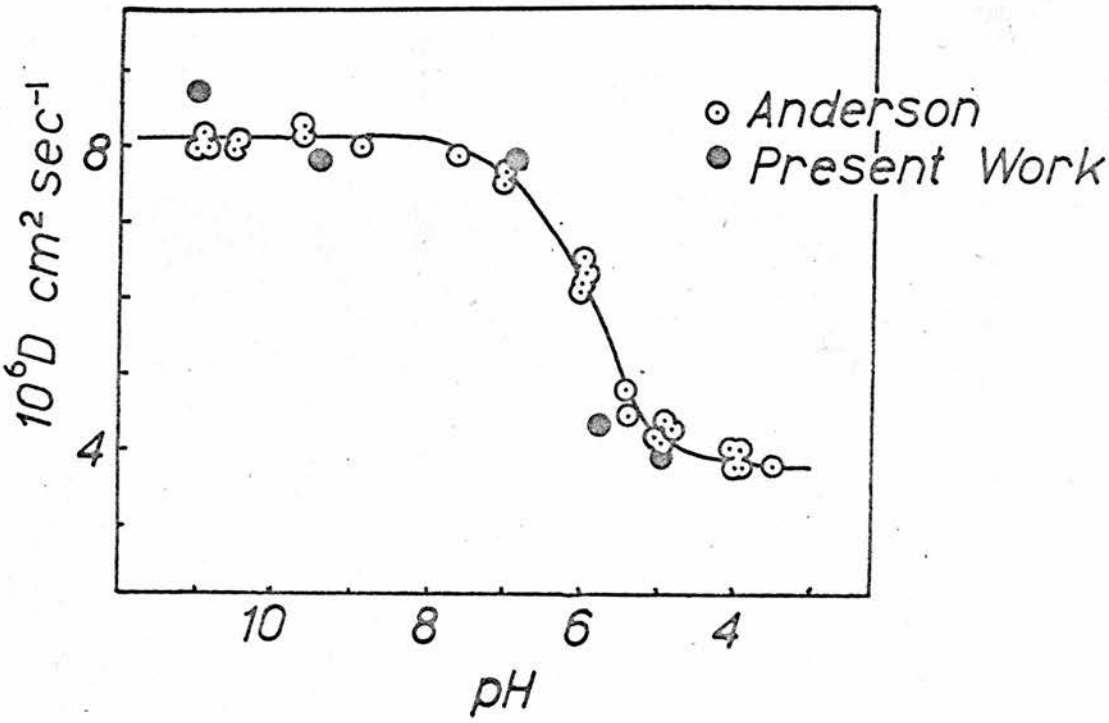


Figure III.

Self Diffusion of Tungstate Ion.



this effect was negligible. The cell was closed by attaching a ground glass cover slip to the lower, flat end by a plastic cement. In strongly alkaline solutions, this cement decomposed. A glass seal was then considered advisable and the cell was closed by melting the lower end and pressing it flat. To minimise the errors involved due to non-uniformity of the cells, which might occur during melting, the cells were made 5 cms. long. Using cells of this length, the diffusion equation could be solved only by successive approximation, unless the diffusion was allowed to proceed for a period of not less than twelve days, as the term Dt/l^2 would not be sufficiently large to allow the second and subsequent terms of the diffusion equation to be neglected without causing an error of more than one percent in the value of the diffusion coefficient. It was found that cell distortion could be considerably reduced if the cells were sealed by placing a drop of molten pyrex over the hole in the foot of the tube, which had been heated almost to melting. This enabled the 2 cm. cells to be used. The cell length was measured by a micrometer so that the cell volume could be determined.

To ensure correct functioning of the Geiger counter and associated equipment, the plateau of the count against applied voltage curve was checked, and quality control charts were constructed using a carbon-14 source. These were all satisfactory.

The extent of washing required to remove completely all the active solution from the cells was determined. The cells were

filled with an active solution, emptied, and then washed by filling them with distilled water and transferring each successive washing to an aluminium planchet, using a capillary pipette. Each washing was counted separately, and it was found that, in all cases, the third wash contained less than one percent of the total activity, and that no activity could be detected in the fourth and subsequent washings. The capillaries were tested in each case for residual activity after washing, to see if the active ions were adsorbed on the cell walls. No residual activity was found, and it was concluded that four washings would give quantitative transfer of the cell contents to the planchet.

Small volumes of active solution were measured by an Agla micrometer syringe.

Mills (1953) stated that a pH difference between tracer and bath solutions caused large errors in the value of the diffusion coefficient. He suggested that the effect was related to the very high diffusion coefficient of hydroxyl and hydrogen ions. Consequently, great care was taken to ensure that the pH values of active and bath solutions were identical.

To test the apparatus and techniques required for this method, Anderson's (1949) self diffusion coefficients of tungstate ions in solutions of various pH values, were repeated.

The solutions for diffusion were prepared from sodium tungstate solution, 0.0025 molar in tungsten. The quantity of stock active solution, containing the tungsten-187 isotope in

sodium hydroxide solution, which was required to give suitable activity (about 5000 counts per hundred seconds for 0.01 ml.) to the labelled solution, was added to a 50 ml. sample of the sodium tungstate solution. This made the concentration of tungsten slightly higher in the labelled solution than in the bath solution, which, according to Anderson (1949), was necessary to suppress convection effects. The pH of the labelled solution was measured and the bath solution was prepared by adjusting 100 ml. of the inactive sodium tungstate solution to the same pH.

The active solution, prepared above, was used to prepare labelled solutions of different pH for other diffusion experiments, the bath solution being adjusted to the corresponding pH in each case. Solutions, 0.0025 molar in tungsten, containing hydrochloric acid, or sodium hydroxide, were used for pH adjustment so that the tungsten concentration would remain unchanged.

The bath solution was placed in the beaker, and immersed in a 25°C thermostatic water bath. A rubber stopper was placed in the neck of the beaker to prevent carbon dioxide absorption by the solution. After about one hour, when the bath solution had reached 25°C, the carrier, with four cells filled to overflowing with the active solution, was gently lowered into the bath until only the tops of the cells remained above the surface. The apparatus was left like this for two hours, to minimise convection currents caused by temperature differences inside the assembly, and then the cells were gently lowered into the bath until their tops were at a depth of about 2 cms.. The diffusion was allowed

to proceed for about 48 hours.

The cells were removed from the bath and the active solutions, plus washings, were transferred to planchets. Five standard samples of the original active solution were measured out and all the samples were gently dried under an infra-red lamp. When dry the activity of each sample was measured. Since the volume of each cell is known, the count which it would have given before diffusion can be calculated from the standard.

Each result given below is the average of that obtained for the four cells. They are plotted on figure III with Anderson's results and the agreement is good.

pH	D x 10^6 cm^2 sec^{-1}	Standard deviation	%
11.10	8.74	0.378	4.3
9.45	7.82	0.360	4.6
6.90	7.87	0.094	1.2
5.80	4.36	0.273	6.3
5.02	3.70	0.427	11.5
		Average	= 5.6

During these experiments it was noticed that a considerable quantity of water had evaporated from the bath solutions and condensed on the rubber bung. This increases the concentration of salts in the bath solution and will suppress diffusion from the cells. If drops of this condensed water were to drip back

into the bath solution, they would introduce a concentration gradient producing unpredictable errors. To minimise this effect, the temperature was reduced to 20°C, which was just above room temperature, thus reducing evaporation and condensation. A larger volume of bath solution was also used so that the air space above it was reduced to a minimum. Since effects due to evaporation and condensation are smaller at the foot than at the top of the bath, the cells were lowered as far as possible, so that the tops of the cells were at a depth of about six cms.

The self diffusion coefficients of tungstate ions in solutions of the same pH and concentration at different temperatures were found to determine the magnitude of the effect of temperature on the self diffusion coefficient.

Temperature °C	20	25	30
$D \times 10^{6}$ cm^{2} sec^{-1}	5.43	6.41	6.70
Standard deviation	0.275	0.089	0.163

This shows that the effect of temperature is not large, of the order 2 percent per centigrade degree. The thermostat in use was accurate to ± 0.2 centigrade degrees, giving a possible error in D, due to temperature, of ± 0.4 percent, which is well within the accuracy of the method.

Self diffusion of tantalate anions

Three series of experiments were carried out. In the first series, the active solution, 0.0025 molar in tantalum, was

prepared directly from a stock active solution of potassium tantalate in potassium hydroxide, containing the tantalum - 182 isotope, using sodium bicarbonate as buffer. The bath solution of the same concentration was prepared from potassium hexatantalate solution, and buffered with the same concentration of sodium bicarbonate. The buffer was used to reduce the pH, since mineral acids give immediate precipitation with tantalate solutions. The lowest pH, keeping the solutions free from precipitation, which was obtained by this method was 10.55. The bath solution was adjusted to this pH by a solution, 0.0025 molar in tantalum, containing potassium hydroxide, which was also used in all subsequent pH adjustments.

Samples from diffusion experiments at high pH gave greatly reduced counts, because, while the sample for counting was being prepared, the strong potassium hydroxide absorbed carbon dioxide and formed potassium carbonate, which absorbed radiation. This was partly overcome by diluting the samples with water so that the sample was spread over the planchet. This avoided a thick spot in the centre of the planchet and higher counts were achieved.

The results given below are plotted in figure IV.

Figure IV.

Self Diffusion of Tantalate Ion.

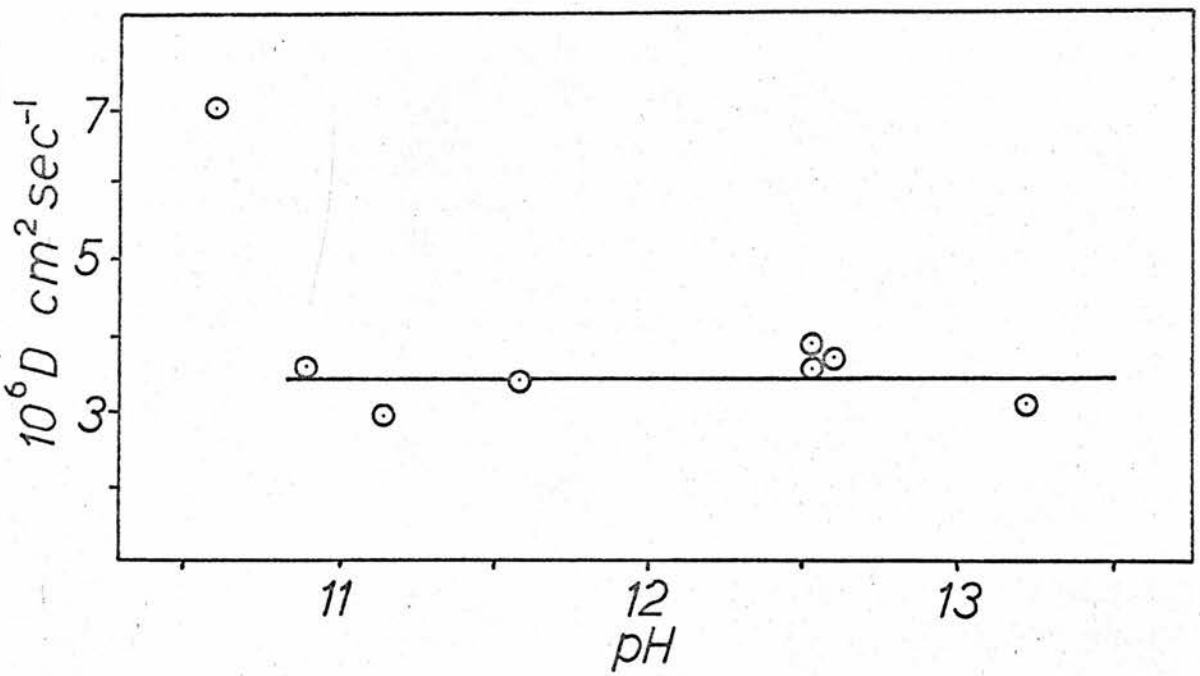
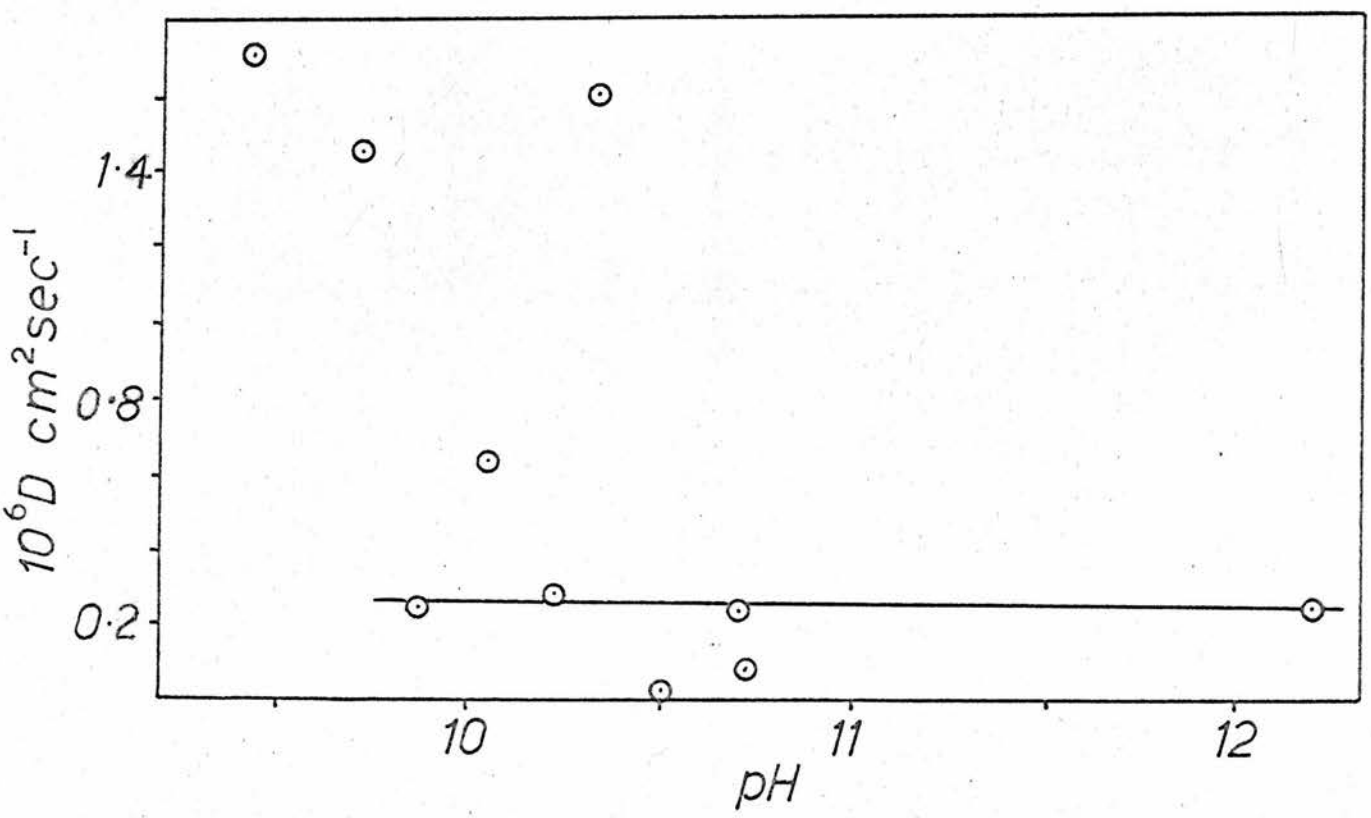


Figure V.

Self Diffusion of Tantalate Ion.



pH	D x 10^6 cm^2 sec^{-1}	Standard deviation	
		σ	%
10.55	6.94	0.544	8
10.85	3.56	0.581	16
11.10	2.92	1.407	48
11.55	3.39	0.159	5
12.50	3.93	0.553	14
12.50	3.71	1.118	29
12.50	3.60	0.709	20
13.20	3.12	0.608	20
		Average	20

In the second series, the active solution was prepared by adding a small quantity of highly active stock tantalate solution to an inactive solution, 0.0025 molar in tantalum. In this series it was found that stable solutions of much lower pH could be obtained, by using potassium bicarbonate, instead of sodium bicarbonate, as buffer.

To find out if the pH of the bath solution remained constant, this was measured before and after diffusion in this series.

The results, given below, are plotted in figure V.

pH		$D \times 10^6 cm^2 sec^{-1}$	Standard Deviation	
before	after		σ	%
9.41	9.31	1.67	1.630	98
9.71	9.61	1.45	0.552	38
10.04	10.14	0.63	0.540	86
10.22	10.16	0.29	0.058	20
10.32	10.00	1.60	0.292	18
10.50	10.28	0.019	0.014	74
10.70	10.40	0.24	0.136	57
12.20	12.00	0.26	0.112	43
			Average	54%

In a third short series, fresh solutions were prepared at pH 9.86 in the same way as in the second series and these were allowed to stand for four days before diffusion was started.

The results are also plotted on figure V.

pH		$D \times 10^6 cm^2 sec^{-1}$
before	after	
9.86	9.81	0.25
10.72	10.60	0.09

The accuracy of the diffusion coefficients obtained for tantalate ions is less than that obtained for tungstate ions.

This is probably due to the instability of tantalate solutions, and to pH change during diffusion.

Spectra

Potassium tantalate solutions absorb strongly in the region below 3000 Å, due to a charge transfer band having a maximum below 2100 Å, the lower limit for the Unicam S.P. 500 spectrophotometer used in this investigation. Since the position of maximum absorption was unobtainable, the absorption edge was found for a solution, 0.00084 molar in tantalum, of varying pH.

The pH of this dilution of potassium tantalate is 10.16, which was raised by adding small amounts of sodium hydroxide solution, for which an absorption correction was applied at pH 11 and above. Sodium hydroxide became the major absorbing species above pH 11.83, making results in this region inaccurate. Since mineral acids gave immediate precipitation on addition to tantalate solutions, the pH was lowered below 10.16 by carbon dioxide, to delay the precipitation long enough for a spectrum to be measured in all cases where the pH was 5.5 and above.

Figure VI shows a plot of absorption edge against pH. The absorption edge is constant at 2380 Å in the pH region 8. to 11.83 and at 2570 Å below pH 7.

Figure VI.

Dependence of Absorption Edge on pH.

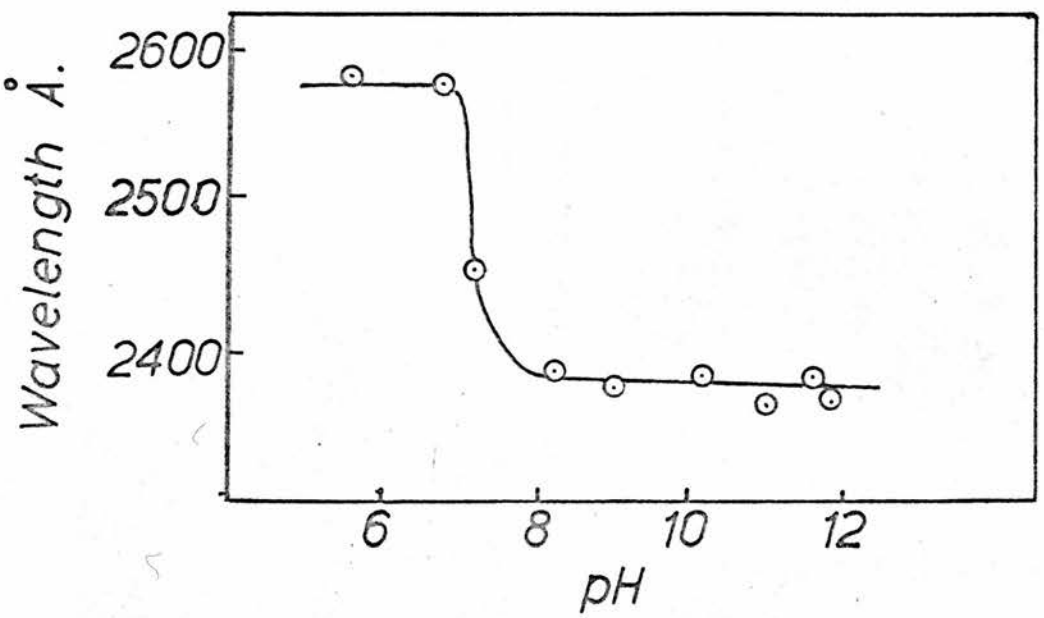
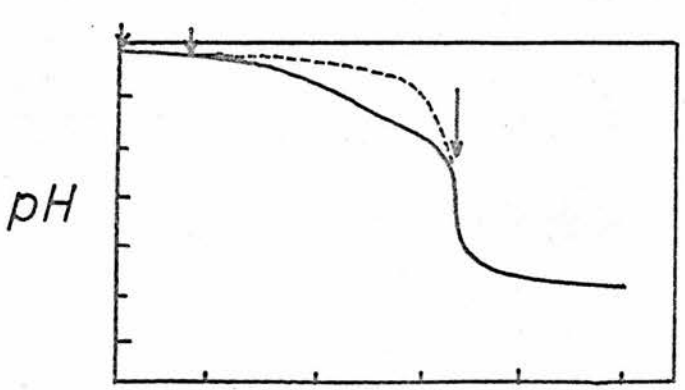


Figure VII.

Potentiometric Titration of Tantalate Solution, from Britton and Robinson (1933).



Potentiometric titrations

Studies of the precipitation of tantalum pentoxide from potassium hexatantalate solutions with hydrochloric acid [Peirce and Yntema, 1930] showed that precipitation began at pH 7.89 and was complete at pH 2.81. Britton and Robinson (1933) carried out this titration and their results (figure VII) showed no evidence of any species, other than hexatantalate, in solution, and indicated greater hydrolysis than was found by Peirce and Yntema.

Potentiometric titrations of potassium hexatantalate solutions were conducted at room temperature, in an atmosphere free from carbon dioxide using a wide range glass electrode and a calomel electrode, in conjunction with a Marconi extended scale type pH meter, T.F. 1093. The apparatus is shown in figure VIII. To minimise local high concentrations of titrant, a fast magnetic stirrer was used. The tip of the semi-micro burette was placed near the centre of the titration vessel so that the titrant would be rapidly dispersed.

The potassium tantalate crystals were dissolved in boiled-out distilled water to prevent contamination of the solution by carbonate.

Titrations with hydrochloric acid of 1 to 2 g. potassium hexatantalate crystals dissolved in 100 ml. water gave unrepeatable potentiometric curves. Titrations using smaller samples, 0.1 to 0.2 g, gave curves (figure IX) which were similar, but not identical. The speed of titration was thought to be the main

Figure VIII.
Apparatus for Potentiometric Titrations.

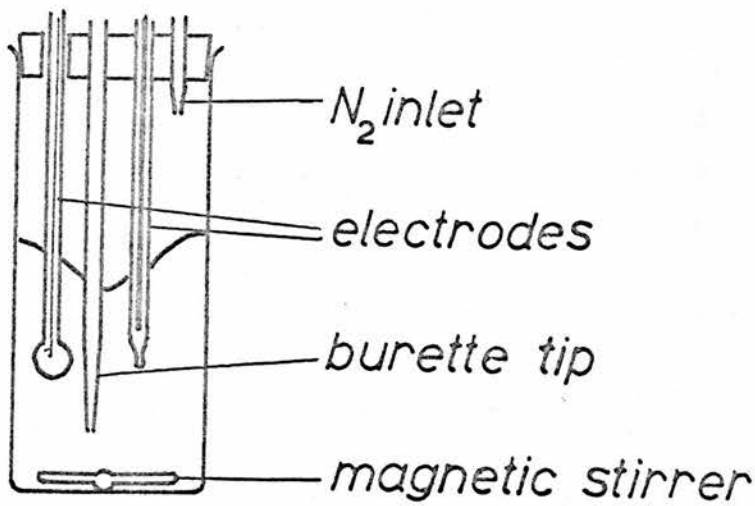


Figure IX.
Potentiometric Titration of Tantalate Solution with Acid.

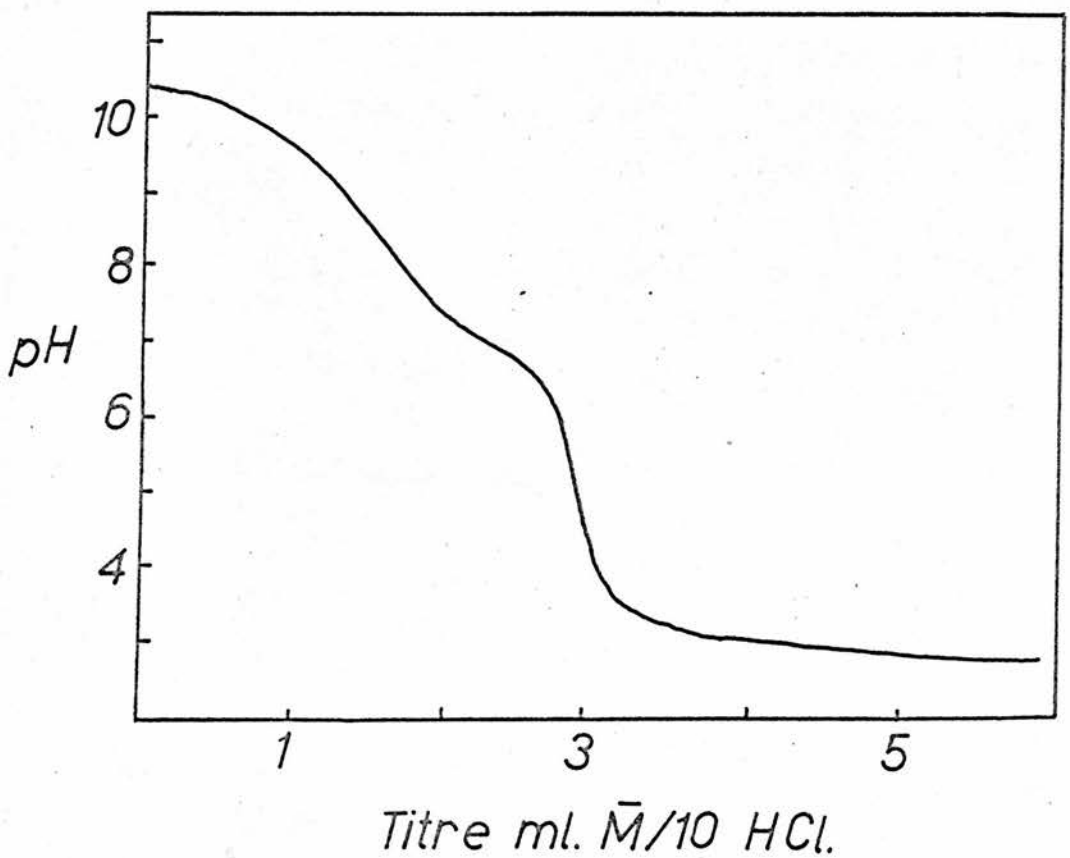


Figure X.
Back Titration.

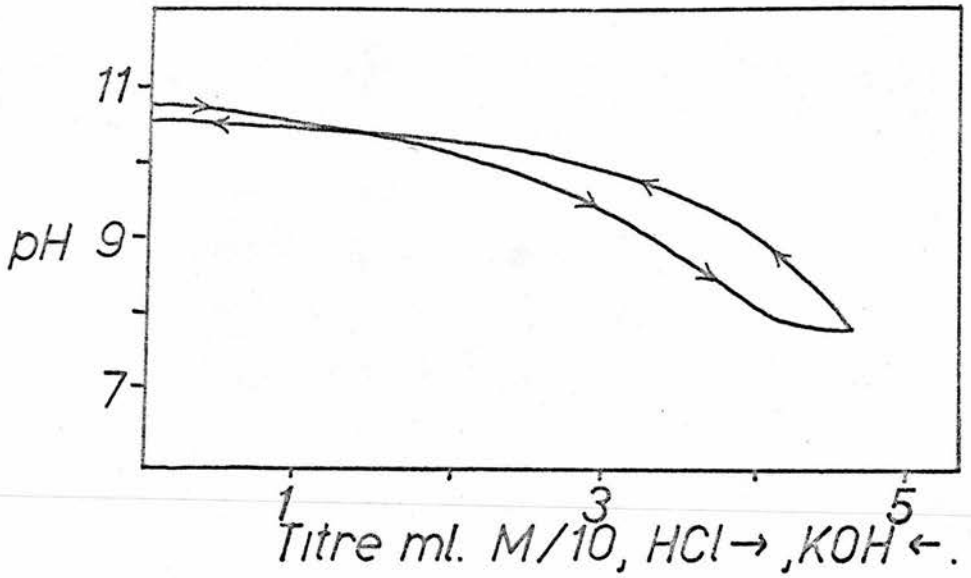
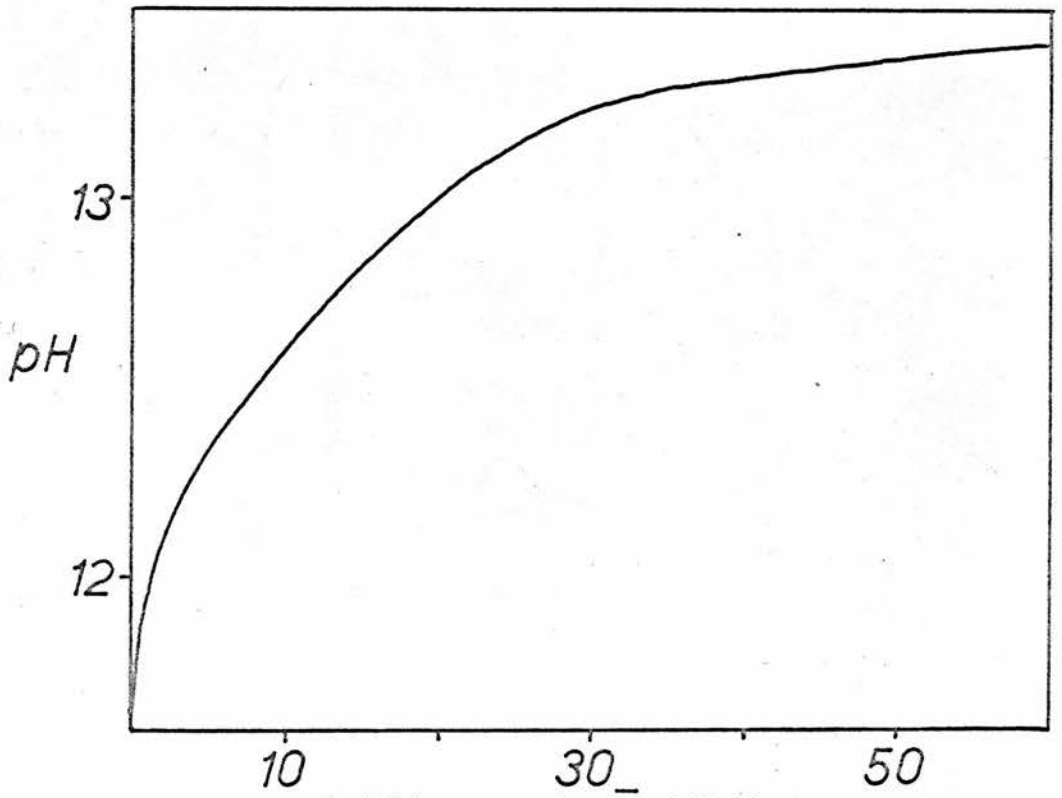


Figure XI.
Potentiometric Titration of Tantalate Solution with Alkali.



factor preventing consistent results as, in one titration, where five minutes were allowed between each 0.1 ml addition of decinormal hydrochloric acid, sharper end points were obtained. These titrations all indicated a flat portion around pH 8, to which point a titration was carried out, attempting to measure the equilibrium pH after each addition of acid. This was done by measuring the pH at one-minute intervals, and delaying the addition of acid until three consecutive values were the same. To determine if this part of the titration was reversible, a back-titration was carried out with decinormal potassium hydroxide. In this back titration, equilibrium was reached very quickly. The solution, which became milky during titration, did not clear during or after the back titration. The result is given in figure X. This experiment was repeated, but before the back titration was started, the solution was allowed to stand for three days, during which time the pH rose by 0.8 pH units, showing that equilibrium had not been attained during previous titrations.

A solution of potassium hexatantalate was titrated with molar potassium hydroxide in an attempt to obtain evidence for depolymerisation products. The result is shown in figure XI.

Discussion

The first series of diffusion results shows that the diffusion coefficient is constant from pH 10.8 to 13.2, which is in agreement with classical diffusion data in this pH range [Jander and Ertel, 1956]. The numerical values are not directly comparable since classical diffusion utilises a concentration gradient and self diffusion does not. The ionic species in the pH region 10 to 12.5 has been shown conclusively to be $[Ta_6O_{19}]^{8-}$ [Nelson and Tobias, 1963, 1964; Aveston and Johnson, 1964], and the value of the self diffusion coefficient, 3.46×10^{-6} cm^2 sec^{-1}, is therefore undoubtedly due to this ion.

The first result in this series, 6.9×10^{-6} cm^2 sec^{-1}, is considerably higher than the others. This may be explained by the existence of a small tantalate anion in the strongly alkaline (0.7 molar potassium hydroxide) stock active solution obtained from Amersham. If, on reducing the pH, the rate of condensation of this ion to the hexatantalate is slow, then, since the first experiment was started soon after preparing the active solution from the Amersham stock, the small ion originally present would diffuse from the cell quickly, giving an artificially high value for the self diffusion coefficient. Experiments carried out when the active solution has stood for some time after preparation will not be affected by this, as equilibrium will have been attained, and a true value will be obtained for the self diffusion coefficient. The value obtained in the first experiment in this series will not

be a measure of the self diffusion coefficient of the simple anion, since a concentration gradient is involved, the simple ion not existing in the bath solution. This value therefore gives no information concerning the size of the ion. Despite this, the indirect evidence presented here indicates that another ion, less polymerised than the hexatantalate, exists in 0.7 molar potassium hydroxide solution. Nelson and Tobias (1963) have considered the possibility of a simple tantalate, but found no evidence for this, not even in solutions of pH 13. If the condensation is irreversible, if the rate of depolymerisation is slow, or if solutions of pH 13 are not sufficiently alkaline to depolymerise the hexatantalate, then no evidence for the simple anion can be expected.

All tantalate solutions used in this investigation precipitated on standing. If, therefore, depolymerisation of the hexatantalate took place slowly at pH 13, direct evidence for a simple ion could not be obtained, as the tantalate solutions would probably precipitate before complete depolymerisation had occurred. If, on the other hand, decondensation only took place in solutions of pH above 13, then, because of difficulties in measuring the radioactivity in such solutions, as discussed previously (p. 13), direct evidence from diffusion studies would probably be unobtainable.

Nelson and Tobias (1963) suggest that a mononuclear tantalate anion is unlikely, because a TaO_6^{7-} ion would have too high a

charge for the species to be stable, and a TaO_4^{3-} ion would not have the coordination number of six for oxygen, which tantalum has in all other comparable compounds. However, a mononuclear tantalate anion formulated as $TaO_4^{3-} 2H_2O$ would both have a charge of reasonable magnitude and be six coordinate. The indirect evidence given here may be taken to indicate this, or a similar ion.

The second series of diffusion results shows that the diffusion coefficient is approximately constant, at about 0.26×10^{-6} cm^2 sec^{-1}, from pH 9.8 to 12.2. Using Riecke's (1890) relationship to find the approximate molecular weight, by comparison with the hexatantalate, the molecular weight of the diffusing species is of the order 350,000. Riecke's relationship has been severely criticised by Baker and Pope (1960) who state that for polyanions, diffusion data give completely unreliable estimations of ionic weight. However, since the ratio of the diffusion coefficients, 3.46 to 0.26, is so great, the diffusing species is certain to be vastly greater in size than the hexatantalate, and will probably be a colloid. This colloid is formed in this series, instead of the hexatantalate, because the initial pH was lower than in the previous series. Once formed, the colloid did not form the hexatantalate on raising the pH.

As in the first series, the first two or three points are high, and these can again be explained by non equilibrium

conditions. This does not give any indication of the rate of condensation of the hexatantalate to the colloid, since the formation of hexatantalate from the simple ion occurs slowly.

The third series of diffusion results supports the theory of non-equilibrium solutions given above, since no high results were obtained after allowing the solutions to stand for four days before commencing diffusion.

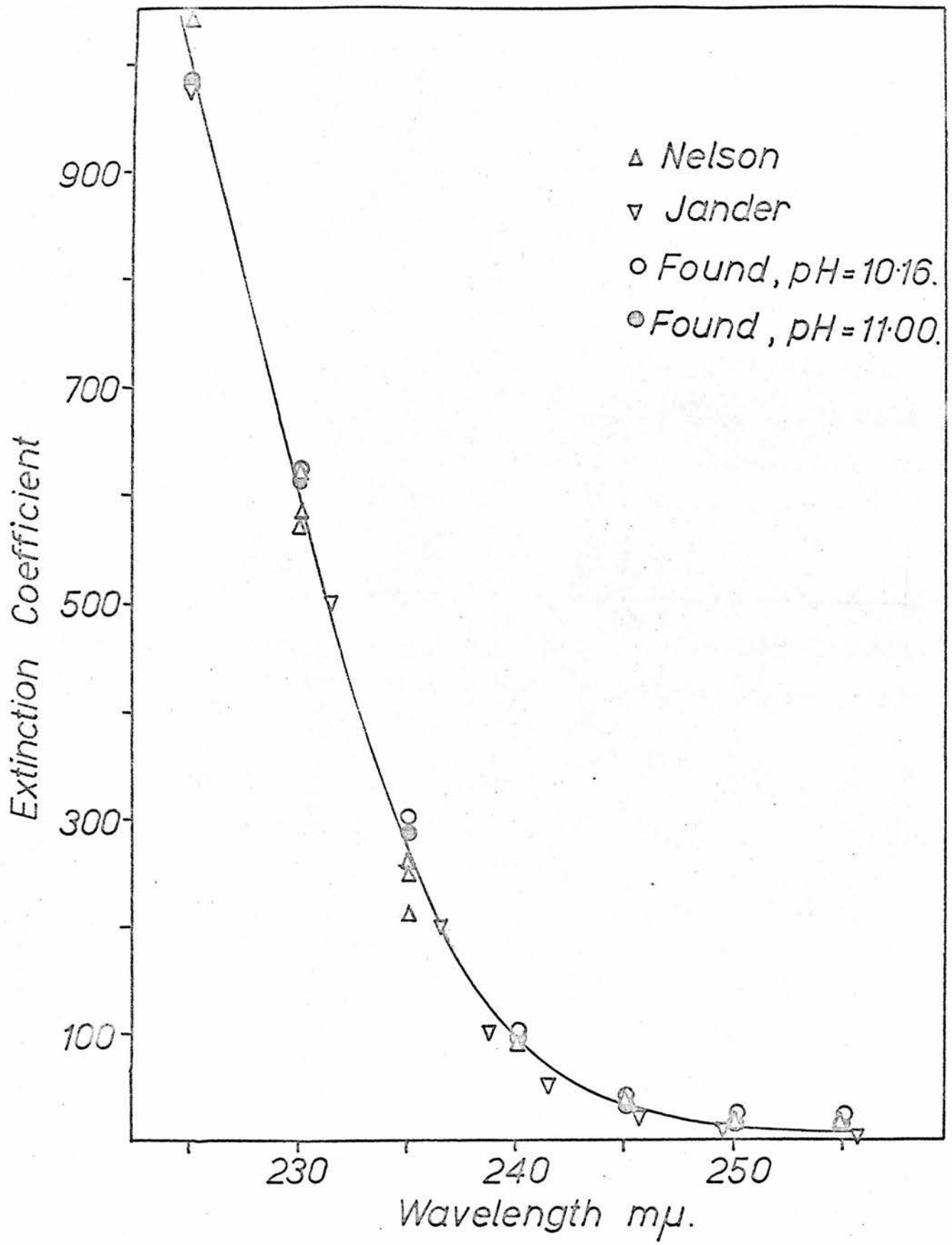
Graphs of extinction coefficient against wavelength for tantalate solutions of different pH are given in figure XII and compared with the results of Nelson and Tobias (1963) and Jander and Ertel (1956).

The position of the charge transfer band of molybdates has been shown to change with the degree of condensation [Lindqvist, 1951]. By analogy, this should occur with tantalates, so that the constancy of the absorption edge position would indicate that the hexatantalate exists in solutions of pH 8 to 11.83. This is in apparent contradiction to the diffusion results which show that a colloid is formed at pH 9.8. Solutions of pH below 10.16 precipitated on standing, after the spectrum had been measured, and they were therefore not at equilibrium during the study. The rate of formation of the precipitate was dependent on the pH of the solution, a precipitate being formed almost immediately in the solution of pH 4.7.

Britton and Robinson (1933) have shown that hydrochloric acid precipitates tantalum pentoxide from tantalate solutions at a uniform rate throughout titrations. This is substantiated

Figure XII.

Spectra of Potassium Tantalate Solutions.



by the failure of solutions to clarify during back titration from pH 8. The tantalum pentoxide is probably precipitated in regions of low pH, which will exist immediately after the addition of acid. The apparent end point, indicated in figure IX at about pH 8, is probably a consequence of the non equilibrium conditions, which have been shown to exist in this region. No conclusions, regarding the existence and nature of any species more condensed than the hexatantalate, can therefore be drawn from these potentiometric titrations.

The ionic species $[Ta_5O_{16}]^{7-}$, $[TaO_4]^{3-}$, and $[TaO_6]^{7-}$ can only be formed by depolymerisation of the hexatantalate, and evidence for their existence could only be obtained in the pH region above that of hexatantalate solutions. No evidence was found, by potentiometric titration (figure XI), for any ion less polymerised than hexatantalate in the pH range 11.6 to 13.4.

In conclusion, self diffusion measurements have given the range of stability of the hexatantalate anion to be pH 10.8 to 13.2. At lower pH values the hexatantalate has been shown to condense to a colloid. Indirect evidence has been obtained for the existence of an anion, less condensed than the hexatantalate, in strongly alkaline solutions of potassium hydroxide. Ultra violet absorption studies have partly confirmed the range of stability of the hexatantalate anion, but neither spectra nor potentiometric titrations gave evidence of any other species in solution.

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PART 2

Solid Transition Metal Molybdates, Tungstates and Uranates

Introduction

There is very little information concerning the molybdates of transition metal groups IIIA to VIA. Only the compounds of formula $3Y_2O_3 \cdot MoO_3$ [Aitken et al., 1964], and $ZrO_2 \cdot 2MoO_3$ [Doyle and Forbes, 1965] have been characterised; also Goldschmidt (1960) states that niobium (V) oxide and molybdenum (VI) oxide do not react. It was decided therefore to investigate the possible formation of molybdates in these groups, by heating mixtures of the constituent oxides in the solid state. Characterisation was carried out by X-ray diffraction and, in the case of the chromium (III) oxide-molybdenum (VI) oxide system, by the diffuse reflectance method developed by Doyle and Forbes (1965).

In recent years the structures of some anhydrous sulphates and tungstates of copper (II), nickel (II), cobalt (II), iron (II) and manganese (II) have been elucidated by X-ray diffraction. In the anhydrous sulphates of copper (II) [Kokkoros and Rentzeperis, 1958], nickel (II) [Dimaras, 1957], cobalt (II) [Pistorius, 1961], and iron (II) [Coing-Boyat, 1959] and in anhydrous nickel (II) tungstate [Keeling, 1957] it has been

shown that the transition metal ion is surrounded by six oxygens arranged in an octahedron of varying degrees of distortion. It is known that anhydrous manganese (II) sulphate is isostructural with iron (II) sulphate [Pistorius, 1960], and that the anhydrous tungstates of manganese (II), iron (II), cobalt (II) and nickel (II) are isostructural [Keeling, 1957]. There is little structural information about the anhydrous molybdates of the transition metals; Smith (1962) has shown that the anhydrous molybdates of nickel (II) and cobalt (II) are isomorphous, having a pseudo-tetragonal structure-true symmetry monoclinic, but they have a different crystal structure from the corresponding tungstates. It was therefore of interest to examine the spectral and magnetic properties of the anhydrous transition metal molybdates to determine if the transition metal ion is octahedrally coordinated by oxygen as in the sulphates and tungstates. For comparison, the spectral and magnetic properties of the sulphates and tungstates were also determined. An attempt was made to prepare the corresponding anhydrous chromates and uranates, and to study their magnetic and spectral properties and so complete this series of group VI oxy anions.

Experimental Methods

Oxides used in preparations were preheated to the reaction temperature to ensure the absence of volatile impurities, and weighed out in the required proportions. The mixtures were thoroughly mixed and ground in an agate mortar. Where inert or other atmospheres were required, reaction was carried out in platinum crucibles in a Vitrosil tube which was heated in a tube furnace at temperatures up to 1,000° C. Furnace temperatures up to 1,000° C were controlled by Gallenkamp on/off controllers and measured by a chromel/alumel thermocouple in conjunction with a Doran thermocouple potentiometer. This showed a variation of ± 4 Centigrade degrees from the mean at 700° C due to the controller. Platinum vessels were used throughout except in cases where they were attacked, notably by the lower oxides of titanium. Preparations at temperatures over 1,000° C were carried out in alumina boats in a ceramic tube which was heated in a platinum wound resistance furnace giving temperatures up to 1,350° C. The temperature was controlled by an energy regulator and measured by a platinum/platinum-iridium thermocouple with the Doran potentiometer.

X-ray d spacings were obtained by powder photography using a Unicam 9 cm. camera. The X-ray source was a copper target using a nickel filter giving only CuK_{α} radiation of wavelength 1.5418 Å. Well ground samples were held in lithium borate glass

or polythene capillary tubes. Line intensities were estimated visually and expressed relative to the strongest which was taken as 100. The error in d spacings obtained was not more than 0.6% for d spacings less than 1, up to 3% for d spacings of 4Å, this being the maximum error due to measurement. In all cases where comparisons could be made with literature values, agreement was within this range. More accurate d spacings were obtained using a Philips X-ray diffractometer where the error in measurement was about one third of that from powder photographs. This could be improved by running the trace at a scan speed slower than the usual 2 degrees per minute. Using this instrument, the sample was mounted as a thin layer on a vaseline film supported on adhesive tape. CuK_{α} radiation was also used with this apparatus, which was calibrated with a silicon sample. Intensities, measured as peak height, were expressed relative to the highest, again taken as 100. It was essential that the sample be well ground since with many substances, the pattern changed with grinding as shown below for vanadium (IV) oxide

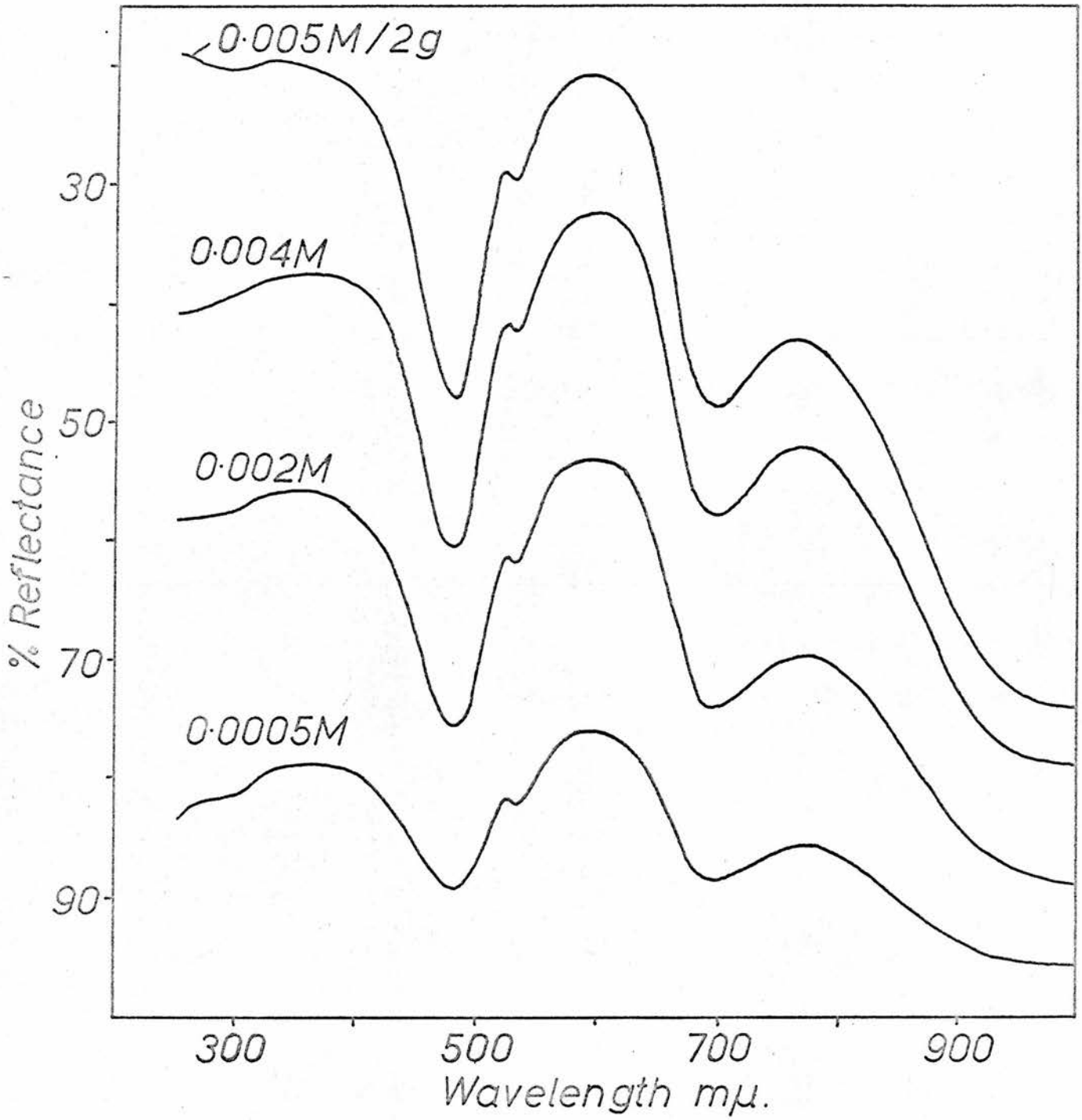
Unground		Ground - large sample		Ground - small sample	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.53	17	3.52	10	3.53	7
3.41	10				
3.32	28	3.32	15	3.33	23
3.22	48	3.21	100	3.22	100
3.08	17			3.09	4
2.979	14	2.989	7	2.979	5
2.430	100	2.436	4	2.436	27

Weight changes on heating mixtures, in the preparation of uranates, were observed on a Stanton Massflow thermobalance where various atmospheres could be used.

A Unicam S.P. 500 spectraphotometer with an S.P. 540 diffuse reflectance attachment was used to measure the spectrum of compounds in the solid state, in the wavelength region 225 to 1,000 mμ. Using this attachment, monochromatic light irradiates a flat sample surface. The diffusely reflected light is directed to the photocell by a spherical mirror, and the intensity is compared with that given by a standard non absorbing surface, in this case magnesium oxide, which was also used as diluent for each sample. Measurements were made on mixtures of 0.003 moles of the substance with magnesium oxide, giving a total weight of 3 g. This mixture gave convenient absorptions in all cases except that of anhydrous manganese (II) sulphate, where since the absorption was so weak, the pure sample was used to obtain features. The mixture of the sample with magnesium oxide, and the magnesium oxide used as standard, were ground for about 15 minutes before measuring the spectrum. The position of the spectral features do not change with the ratio of sample to magnesium oxide in the mixture. This was shown for cobalt (II) tungstate; see figure 1. Each surface under test was prepared by putting the sample into the holder and using a rubber bung to remove the excess and to smooth the surface.

Figure 1.

Cobalt(II) Tungstate Spectra at Various Dilutions.



Magnetic susceptibility was measured by the Gouy method at room temperature using a Newport Instruments, 4 inch, water cooled electromagnet, with associated current regulator and power supply and a Stanton S.M. 12 semi micro balance. The field strength could be varied using this magnet and measurements were made over an approximately 5 fold range of field strength. No field dependence was observed (see appendix I) showing the absence of ferromagnetic impurities. Mercury (II) tetrathiocyanatocobaltate (II), $Hg[Co(SCN)_4]$, was used for calibration [Figgis and Nyholm, 1958]. The magnetic susceptibility was calculated from

$$10^6 X \text{ c.g.s. units} = \frac{\alpha + \beta F^1}{w}$$

where α and β are constants for the apparatus,

F^1 is the force on the sample in the magnetic field in mg., corrected for the diamagnetic force on the tube

and w is the weight of the sample in g..

The calibration was checked by measuring the magnetic susceptibility of copper (II) sulphate pentahydrate. The value obtained was 5.94×10^{-6} c.g.s. units, which compares favourably with the value given by Figgis and Lewis (1960) - 5.92×10^{-6} c.g.s. units. Effective magnetic moment was calculated from the Curie Law,

$$\mu eff = 2.84 \, (Xm^1 \, T)^{\frac{1}{2}} \text{ Bohr magnetons}$$

where T is the absolute temperature of the sample during measurement and Xm^1 is the molar susceptibility (X x M) corrected for the inherent diamagnetic susceptibility of the compound.

The effective magnetic moment was calculated for two samples of each compound, and, excluding the uranates, the results were found to vary by an average of $\pm$ 0.73% from the mean. Figgis and Lewis (1960) state that the use of values of the effective magnetic moment, calculated from the Curie-Weiss law,

$$\mu eff = 2.84\ [Xm^{1}(T-\theta)]^{\frac{1}{2}}\ \text{Bohr magnetons}$$

where θ is the Weiss constant in centigrade degrees, has little physical basis unless anti-ferromagnetic interactions are known to occur. However, when values of θ were available, the Curie-Weiss law was used to compare literature values of effective magnetic moment.

Preparation of Oxides Used as Starting Materials

All reagents used were of the highest purity available. The d spacings of all oxides used as starting materials are given in appendix II where a comparison is made with literature values.

Molybdenum (VI) oxide and tungsten(VI)oxide were commercially available and these were heated to 700 and 1,000° C respectively for 24 hours prior to their use in preparations. Uranium (VI) oxide was prepared by heating uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, at 400° C [Dawson et al., 1956] for 7 days to constant weight. The weight loss was 42.39% (theoretical, 43.03%). Uranium (VI) oxide was also obtained commercially and was found to lose 5.5% of its weight on heating to 300° C for 6 days. The product was brick-red coloured in both cases and showed no trace of dark brown triuranium octoxide. The X-ray powder photograph of both samples gave no lines [Wait, 1955] which proved the absence of triuranium octoxide. Wait (1955) states that the brick-red product has the formula $UO_{2.82}$. Copper (II) uranate was prepared from uranium (VI) oxide from uranyl nitrate, whereas all other uranates were prepared from commercial uranium (VI) oxide heated to constant weight.

The oxides of yttrium (III), titanium (IV), hafnium (IV), vanadium (V), niobium (V) and chromium (III) were available commercially. Titanium (II) and titanium (III) oxides were prepared by heating appropriate quantities of titanium metal powder with titanium (IV) oxide under argon at 1,200° C for

several hours in alumina vessels. Vanadium (III) oxide was prepared by reducing vanadium (V) oxide by hydrogen at 700° C for 4 hours [Frandsen, 1952]. The weight loss was 17.54% (theoretical, 17.59%), and analysis by the method of Wickham and Whipple, (1963) gave the purity as 99.2% vanadium (III) oxide. Vanadium (IV) oxide was prepared by heating an equimolar mixture of vanadium (III) and vanadium (V) oxides in nitrogen at 600° C for 16 hours. On grinding the product, orange spots of unreacted vanadium (V) oxide were observed. The mixture was then heated at 1,000° C in argon for 14 hours. The product appeared homogeneous and a diffractometer trace gave no indication of vanadium (III) or vanadium (V) oxides. Vanadium metal was prepared by reducing vanadium (III) oxide with calcium hydride [Frandsen, 1952]. The mixture was pelleted and heated at 1,200° C for 2 days in argon. The product was washed with dilute hydrochloric acid, then water, and vacuum dried over phosphorus (V) oxide. A sample of the product was analysed by dissolving in acid persulphate and boiling, the vanadium being determined by reduction by sodium sulphite and titration with standard permanganate solution. This analysis gave the purity of the sample as 90.75 and 90.13% vanadium metal. Using this analytical result, vanadium (II) oxide was prepared by mixing the metal with the appropriate quantity of vanadium (III) oxide and heating at 1,300° C in hydrogen for several days, grinding periodically [Todd and Bonnickson, 1951]. A comparison of the d spacings,

obtained from a diffractometer trace, with those given by Mathewson et al. (1932) indicated that vanadium (II) oxide had been obtained, but that it was contaminated by vanadium (III) oxide. Niobium (IV) oxide was prepared by reducing niobium (V) oxide by hydrogen at 1,125° C for 2 days in an alumina boat. The weight loss was 6.41% (theoretical, 6.02%). Oxidation of a sample of niobium (IV) oxide by heating in air at 650° C for 1 hour, gave a weight gain of 6.35% (theoretical, 6.40%). The niobium (V) oxide so obtained had a different crystalline form from the original.

Manganese (II) oxide was prepared by heating manganese (II) carbonate in vacuum at 590° C [Schulek and Pungor, 1960]. Cobalt (II) oxide was prepared by the decomposition of cobalt (II) carbonate in nitrogen at 1,000° C [Chufarov et al., 1950]. Nickel (II) oxide was prepared by melting nickel (II) nitrate hexahydrate, heating to dryness, and igniting at 950° C for 24 hours [Kano and Wakayama, 1948]. Copper (II) oxide was available commercially.

Molybdates of Groups IIIA, IVA, VA and VIA

The X-ray d spacings of all the following reaction products are given in appendix III.

A compound of composition $3Y_2O_3.MoO_3$ has been prepared from the constituent oxides at temperatures above 1,000° C [Aitken, 1964]. No other compound in this system has been reported. In the present work, various ratios of the oxides were heated overnight at 660° C and the weight loss in each case was less than 0.7%. Diffractometer traces of the products showed only two compounds in this system at 660° C of compositions $Y_2O_3.3MoO_3$ and $Y_2O_3.4MoO_3$.

Souchay (1946) states that he has confirmed the non existence of titanium (IV) molybdate from solution reactions. Various ratios of titanium(IV) oxide (anatase) to molybdenum (VI) oxide were heated at 700° C in air for 3 days. The mixtures all became yellow, but diffraction patterns showed that no reaction had occurred in this period, but that some anatase had been converted to rutile.

A mixture of titanium (III) oxide and molybdenum (VI) oxide was heated at 700° C in argon for 1 hour. A diffractometer trace of the product showed molybdenum (IV) oxide, titanium (IV) oxide (rutile) and also 2 additional peaks which may be due to anatase. These facts are in accordance with the following taking place

$$Ti_2O_3 + MoO_3 \rightarrow 2TiO_2 + MoO_2,$$

and the formation of a molybdate of titanium (III) is impossible.

A titanium (II) oxide-molybdenum (VI) oxide mixture was heated at 650° C in nitrogen for 14 hours. A diffractometer trace of the product showed molybdenum (IV) oxide and titanium (IV) oxide (rutile). The titanium (II) oxide was therefore oxidised by the molybdenum (VI) oxide and the formation of a titanium (II) molybdate is impossible.

No report has been given concerning molybdates of hafnium. Hafnium (IV) oxide and molybdenum (VI) oxide were reacted in various ratios for periods between 2 and 5 days at 700° C. The products were white in each case and weight losses were due to molybdenum (VI) oxide volatilisation. Diffraction patterns of the products showed only one compound in this system, of composition $HfO_2.2MoO_3$. The d spacings and intensities of this compound are almost identical to those of the compound $ZrO_2.2MoO_3$, prepared by Doyle and Forbes (1965), indicating that the two are isostructural.

No compounds of molybdenum (VI) oxide with any oxide of vanadium have been reported.

Vanadium (V) oxide was reacted in various ratios with molybdenum (VI) oxide at 640° C in air. Weight losses were small in all cases and an X-ray examination of the products showed only one compound in the series of composition $V_2O_5.MoO_3$.

Various ratios of vanadium (IV) oxide to molybdenum (VI) oxide were reacted in nitrogen at 700° C for 16 hours. All samples showed a slight weight loss. An X-ray examination of the products showed only one compound in this system of composition $VO_2.MoO_3$. This could be formulated as $VO(MoO_4)$, i.e. vanadyl molybdate, comparable to vanadyl sulphate $VO(SO_4)$.

Vanadium (III) oxide and molybdenum (VI) oxide were heated together at 600° C in nitrogen giving a negligible weight loss. An X-ray study of the product indicated molybdenum (IV) oxide. The vanadium (III) oxide must reduce the molybdenum (VI) oxide thus making the formation of a vanadium (III) molybdate impossible.

A mixture of vanadium (II) oxide and molybdenum (VI) oxide was heated at 700° C in nitrogen for 16 hours. A weight gain during heating would have indicated oxidation by oxygen impurity in the nitrogen. This was not found but a slight weight loss, due to molybdenum (VI) oxide volatilisation, occurred. A diffractometer trace of the product gave a pattern due entirely to vanadium (III) oxide. The vanadium (II) oxide must therefore be oxidised by the molybdenum (VI) oxide, making the formation of a vanadium (II) molybdate impossible.

Goldschmidt (1960) found that niobium (V) oxide and molybdenum (VI) oxide did not react, but formed a βNb_2O_5 solid solution. In the present work, various ratios were heated at 660° C in air, but no evidence of compound formation was found from X-ray diffractometer traces.

No report of reaction between niobium (IV) oxide and molybdenum (VI) oxide has been given. This reaction was carried out in nitrogen at 660° C for 2 days. A diffractometer trace of the product, from heating a mixture of the oxides in the ratio $2NbO_2:MoO_3$, gave d spacings, all of which could be accounted for by niobium (V) oxide and molybdenum (IV) oxide. These facts are in accordance with the following taking place

$$2NbO_2 + MoO_3 \rightarrow Nb_2O_5 + MoO_2$$

and the formation of a niobium (IV) molybdate is impossible.

The molybdenum (VI) oxide - chromium (III) oxide system has not been previously investigated. Various ratios of the oxides were reacted at 660° C for 3 hours, reground and reheated for a further 18 hours. X-ray powder photographs indicated only one product of composition $Cr_2(MoO_4)_3$. Sixteen mixtures, containing 0 to 100 mole percent molybdenum (VI) oxide in chromium (III) oxide were reacted as above and the products analysed by the diffuse reflectance method developed by Doyle and Forbes (1965). Plots of mole percent molybdenum (VI) oxide against $(A/R)^{1.383}$ at 740 and 530 mμ. are shown in figures 2 and 3. These show compound formation at 75 mole percent only in the 75-100% range, but are less conclusive below 75%. However X-ray diffraction patterns show only one reaction product of composition $Cr_2(MoO_4)_3$ in this system.

Figure 2.
Reflectance of the Cr_2O_3-MoO_3 System at 740 mμ.

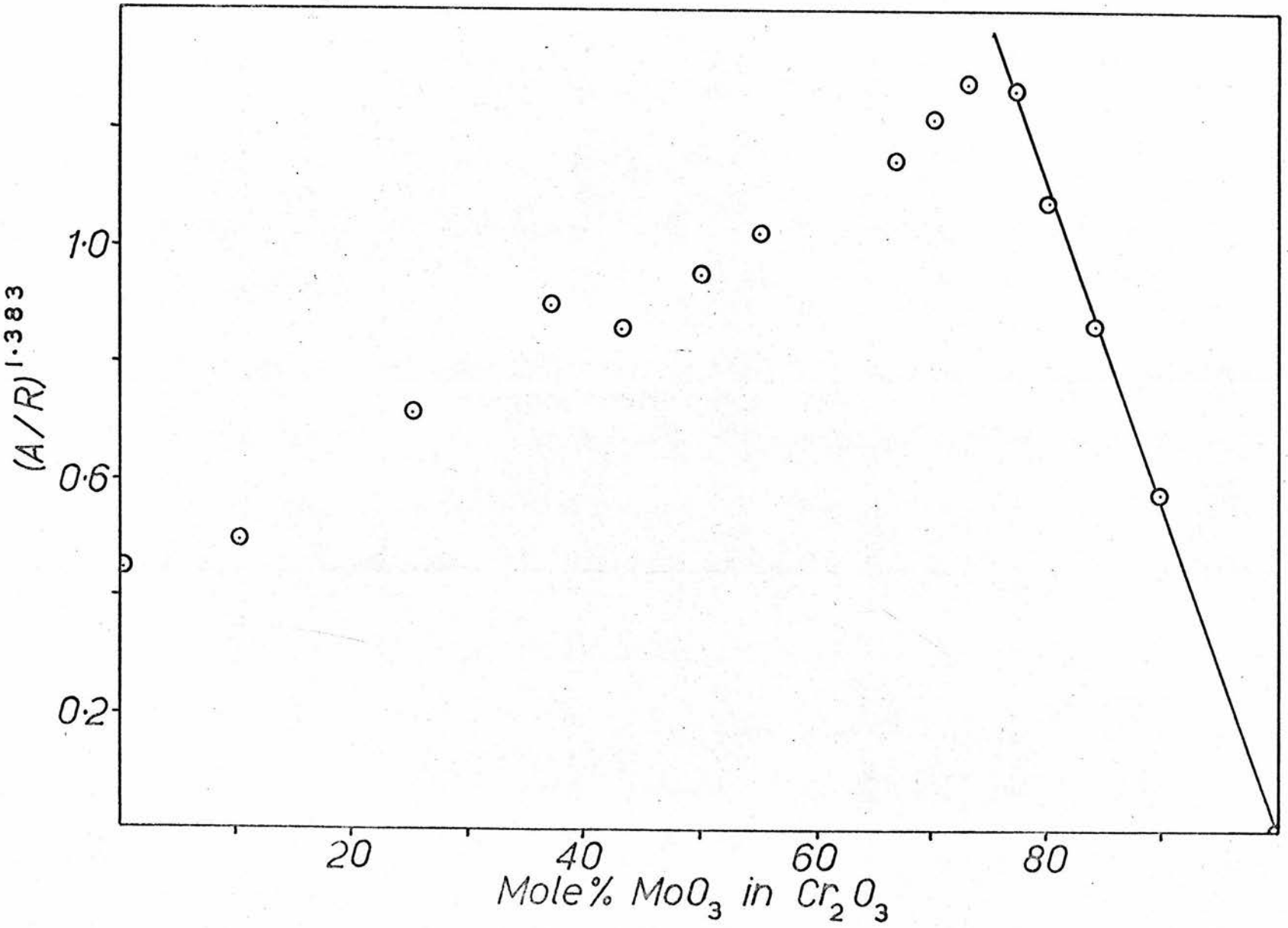
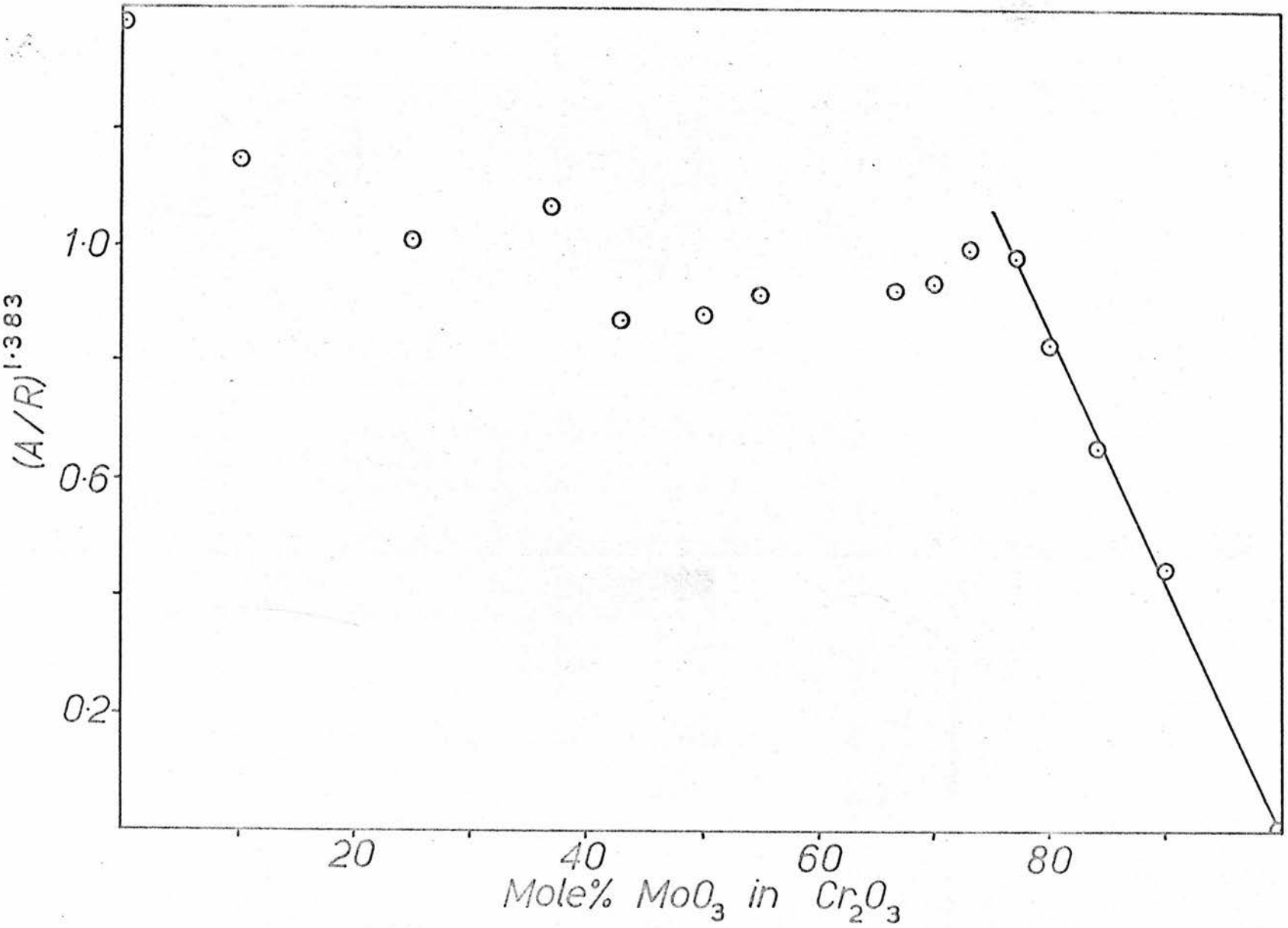


Figure 3.
Reflectance of the Cr_2O_3 - MoO_3 System at 530 mμ.



Bayer (1960) has described the preparation of chromium (III) tungstate, Cr_2WO_6, by heating a mixture of the constituent oxides to 850 to 950° C in air. In the present work, various ratios of the oxides were reacted at 1,000° C for 3 hours in air to determine if this product, obtained by Bayer (1960), is the only one in this system. An X-ray examination of the system showed only one compound of composition Cr_2WO_6 and the d spacings obtained were in agreement with those of Bayer. (See appendix IV).

Sulphates, Molybdates, Tungstates and Uranates of Manganese (II), Cobalt (II), Nickel (II) and Copper (II)

X-ray d spacings of the following molybdates, sulphates, tungstates and uranates are given in appendices III, IV, V and VI respectively.

Anhydrous manganese (II) sulphate was prepared by heating the tetrahydrate at 540° C for three days when weight constancy was attained. The d spacings obtained from a diffractometer trace gave agreement with literature values.

Carlston (1963) found that only one compound exists in the manganese (II) oxide-molybdenum (VI) oxide system, namely $MnMoO_4$, which is stable up to 800° C. In the present work an equimolar mixture was reacted at 700° C in nitrogen for 12 hours giving a weight loss of 0.25%. The product was ground and returned to the furnace for a further 18 hours. The X-ray d spacings have not been previously reported and 3 peaks were observed which were apparently due to molybdenum (VI) oxide. A study of the system by X-ray diffraction showed only one product of composition $MnMoO_4$, and that the lines, which appeared to be due to molybdenum (VI) oxide, were in fact due to the product since they persisted into the manganese (II) oxide rich part of the system.

Karl (1933) prepared manganese (II) tungstate by heating manganese (II) oxide with tungsten (VI) oxide in a sodium chloride flux. In the present work, the preparation was attempted by

heating the constituent oxides at 1,000° C under vacuum. Reaction was complete after 3 hours giving a weight loss of 0.02%. The X-ray diffractometer trace showed no oxides in the product and the d spacings obtained agreed with literature values.

Anhydrous cobalt (II) sulphate was prepared by heating the pentahydrate at 500° C for 7 days to constant weight. An X-ray powder photograph gave d spacings which agreed with the strongest lines quoted in the literature.

Cobalt (II) molybdate has been prepared [Smith, 1962] by precipitation from solution and ignition of the product at 700° C. Forbes (1964) found only one product in the cobalt (II) oxide-molybdenum (VI) oxide system at 700° C. In the present work, an equimolar mixture of these oxides was heated at 700° C in nitrogen for 12 hours. The weight loss was 0.11%. The mixture was ground and reheated to 700° C for 18 hours. The product was lilac in colour but became green on grinding reverting rapidly to lilac on reheating to 700° C. Diffractometer traces of green and lilac samples showed them to be different crystalline forms, neither of which contained oxides. The d spacings obtained for the green sample agreed with literature values.

Cobalt (II) tungstate has been prepared [Batrakov, 1962] by heating cobalt (II) oxide with tungsten (VI) oxide at 600 to 1,000° C. In the present work the preparation was attempted by heating a dry mixture of the oxides at 1,000° C in nitrogen for 24 hours. The weight loss was 0.18%. A diffractometer trace

showed no oxides and agreed with d spacings quoted in the literature.

Cobalt (II) uranate has been prepared [Bertaut et al., 1962] by heating cobalt (II) oxide with uranium (VI) oxide at 900-1,000° C in oxygen. Brisi (1960) obtained the same compound by heating tricobalt tetroxide with triuranium octoxide to 900 to 1,050° C in air. In the present work, the preparation was carried out by heating cobalt (II) oxide and uranium (VI) oxide at 1,000° C in oxygen for 20 hours. The weight loss was 0.75%. A diffractometer trace showed neither cobalt (II) oxide nor triuranium octoxide and agreed with the d spacings obtained by Brisi (1960). Various ratios of the oxides were reacted as above and diffractometer traces of the products showed only one compound in the system, namely $CoUO_4$.

Ostroff and Sanderson (1958) give the decomposition temperature of anhydrous nickel (II) sulphate as 708° C. In the present work the heptahydrate was heated at 500° C to constant weight, which required 7 days. X-Ray d spacings agreed with literature values.

Silvent (1961) found that nickel (II) oxide and molybdenum (VI) oxide react together at 450° C to give one product, $NiMoO_4$, whereas Carlston (1963) found two compounds, $NiMoO_4$ and Ni_2MoO_5, both being stable up to 800° C. This system was studied by X-ray powder photography and by diffuse reflectance [Forbes, 1964] and only one product was found, $NiMoO_4$. An equimolar mixture of the

oxides was heated for one hour at 700° C, which gave a weight loss of 0.15%. The product was then ground and reheated to 700° C for a further 24 hours. A diffractometer trace gave no evidence of constituent oxides, and gave agreement with the literature.

Nickel (II) tungstate has been prepared by heating the constituent oxides [Schwab and Kohler, 1959]. The preparation was carried out in the present work by heating the oxides at 1,000° C for one hour, when the weight loss was 0.07%, regrinding and heating for 18 hours at 980° C. X-Ray diffractometer traces of a series of varying oxide ratios showed only one compound in the series, namely $NiWO_4$, the d spacings of which gave agreement with literature values.

Bertaut et al. (1962) were unable to prepare nickel (II) uranate, and Brisi (1960) found that only one compound of composition NiU_3O_{10} existed in the nickel (II) oxide-uranium (VI) oxide system at temperatures above 500° C. In the present work, the preparation was attempted at 1,000° C in oxygen. An equimolar ratio of the oxides was heated for 30 minutes giving a weight loss of 0.72%. It was then ground and reheated for a farther 2 hours. The product was a chocolate-brown powder. A diffractometer trace showed the existence of a new phase together with a small amount of triuranium octoxide. Another sample of an equimolar mixture of the oxides was heated in oxygen to 1,000° C on a thermobalance and the weight losses and gains were recorded. The mixture was found to lose weight to 700° C and then gain weight rapidly to

840° C where the weight remained constant to 1,000° C. This final weight did not alter on cooling or on reheating to 1,000° C for 45 minutes. The diffractometer trace of this sample gave no indication of excess nickel (II) oxide or triuranium octoxide and gave agreement with the previous sample. Reaction was therefore assumed complete. A sample of nickel (II) uranate was heated at 1,000° C in air for two hours and a diffractometer trace taken of the product. This gave d spacings which corresponded to nickel (II) oxide and triuranium octoxide only, and gave no trace of nickel (II) uranate.

Mallard (1961) states that anhydrous copper (II) sulphate is stable to 670° C whereas Ostroff and Sanderson (1958) give its decomposition temperature as 598° C. In the present work copper (II) sulphate pentahydrate was heated at 660° C for 24 hours when considerable blackening of the product indicated decomposition to copper (II) oxide. The hydrated salt was heated at 500° C and constant weight was attained after 7 days. An X-ray powder photograph gave d spacings which agreed with literature values.

Zelikman (1956) states that the reaction between copper (II) oxide and molybdenum (VI) oxide proceeds rapidly in the temperature range 500 to 600° C. Forbes (1964) obtained only one compound in this system namely copper (II) molybdate, $CuMoO_4$, which he prepared at 700° C. In the present work an equimolar mixture of the oxides was heated at 700° C for 1 hour, giving a weight loss

of 0.23%, ground and reheated for 2 hours. The d spacings obtained from a diffractometer trace gave agreement with those of Forbes and showed no oxide spacings.

Copper (II) tungstate has been prepared by heating a mixture of the constituent oxides at 800° C [Kosek et al., 1961]. This method was used in the present work and the reaction was allowed to proceed for 37 hours. The weight loss was 0.12% and a diffractometer trace gave no d spacings due to copper (II) oxide or tungsten (VI) oxide.

By dissolving copper (II) oxide and triuranium octoxide in concentrated nitric acid, evaporating to dryness and heating the residue to 600° C for 6 hours, Weigel and Neufeldt (1961) obtained copper (II) uranate. The preparation was attempted in the present work by heating copper (II) oxide with uranium (VI) oxide to 1,000° C in air for a few minutes. This gave a weight loss of 2.3%. The sample was then heated to 1,000° C in oxygen for a few minutes, when it gained weight giving an overall weight loss of 0.4%. The reaction was shown to be complete after this very short period of heating by a diffractometer trace which showed no peaks due to copper (II) oxide and only one peak which corresponded to the strongest triuranium octoxide one. Apart from this, most of the other d spacings correspond to those given in the literature.

Attempted preparation of anhydrous chromates

Pelletier et al. (1938) state that solutions of cobalt (II) chloride and potassium chromate give a precipitate of hydrated cobalt (II) chromate on mixing. This preparation was attempted in the present work, the precipitate being dried at 110° C to constant weight. Analysis for cobalt (electrolytically) gave the percentage cobalt as 34.79 and for chromate (by titration with ammonium iron (II) sulphate) as 44.89. The remainder, 20.32% was shown not to be all water since ignition at 1,000° C in nitrogen gave a weight loss of only 12.26%. A flame test proved the presence of potassium. These facts are consistent with the following formulation:- K_2CrO_4. 2.245 $CoCrO_4$. 2.705 CoO. 2.715 H_2O. The preparation of copper (II) chromate was attempted by precipitation from solution in the same way. Qualitative analysis proved the presence of potassium chromate and the precipitate is probably of the same form as the cobalt salt.

Calcium chromate has been prepared [Nishino and Moteki, 1961] by heating mixtures of calcium carbonate and chromium (III) oxide to 1,000° C in air. In an attempt to prepare nickel (II) chromate in the present work, a mixture of nickel (II) oxide and chromium (III) oxide in the ratio 2:1, was heated at 950° C. This gave a weight loss of 0.25% after one day, and heating for three days gave no farther weight change. Since only a weight gain would indicate atmospheric oxidation, nickel (II) chromate cannot be prepared by this method.

Results and Discussion

The room temperature values of measured gram susceptibility and effective magnetic moment are given in table 1. The effective magnetic moments, calculated from the Curie-Weiss law, are compared with available literature values in table 2. Diffuse reflectance spectra are given in figures 4 to 12.

The spectra of copper (II) sulphate, molybdate and tungstate (figure 8) each have a broad absorption band at about 10,000 cm^{-1}, corresponding to the expected single band for a d^9 ion in an octahedral field, and a second band at 32,800, 25,300 and 22,200 cm^{-1} respectively which must be due to charge transfer either from oxygen to copper or within the anionic grouping. The bands at 29,800 and 26,000 cm^{-1} in manganese (II) molybdate and tungstate, 23,200 and 24,100 cm^{-1} in cobalt (II) molybdate and tungstate and at 28,600 and 25,000 cm^{-1} in nickel (II) molybdate and tungstate may be attributed to the same cause. These bands, which are not apparent in the spectra of manganese (II), cobalt (II) and nickel (II) sulphates, may exist further into the ultra-violet, since in both cobalt (II) and nickel (II) sulphate spectra there is strong absorption above 44,500 cm^{-1}.

The manganese (II) ion in a cubic field has the ground state ^6S, this being the only state of multiplicity 6, and all transitions to higher states, of multiplicity 4 or 2, are spin forbidden. All absorptions should therefore be weak. This is so in the case of manganese (II) sulphate, but in manganese (II) molybdate and

Figure 8.

Spectra of Copper(II) Sulphate, Molybdate & Tungstate.

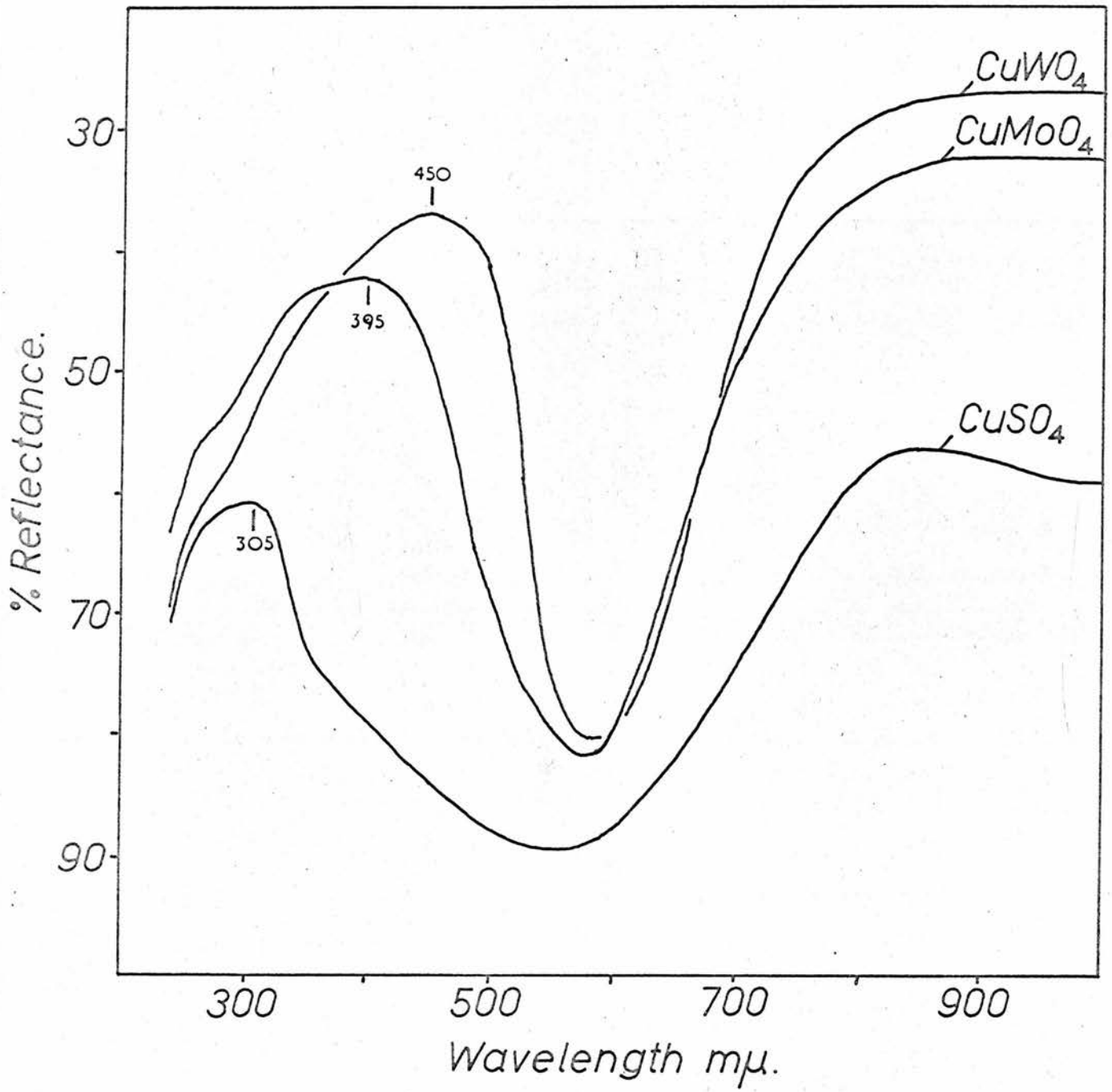


Table 1

Compound	$10^6\chi$(c.g.s. units)		μeff(Bohr magnetons)	
	Sample 1	Sample 2	Sample 1	Sample 2
$MnSO_4$	86.83	90.79	5.56	5.64
$MnMoO_4$	58.08	52.97	5.42	5.17
$MnWO_4$	38.20	39.27	5.22	5.28
$CoSO_4$	63.44	64.74	4.81	4.83
$CoMoO_4$	51.24	50.89	5.14	5.12
$CoWO_4$	31.23	30.80	4.74	4.72
$CoUO_4$	26.89	28.83	4.78	4.93
$NiSO_4$	25.59	26.45	3.04	3.10
$NiMoO_4$	18.51	19.58	3.08	3.18
$NiWO_4$	11.58	12.28	2.89	2.99
$NiUO_4$	6.03	6.28	2.27	2.33
$CuSO_4$	8.53	8.42	1.81	1.80
$CuMoO_4$	6.85	6.87	1.92	1.92
$CuWO_4$	3.99	3.99	1.73	1.73
$CuUO_4$	3.61	3.79	1.78	1.83
$Cr_2(MoO_4)_3$	17.01		3.43	
Cr_2WO_6	19.52	19.98	2.98	3.05
$VO.MoO_4$	3.38		1.34	

Table 2

Compound	θ(C.deg.)	effective magnetic moment (Bohr magnetons)		
		Sample 1	Sample 2	Reference
$MnSO_4$	-24.0	5.78	5.88	5.88 (a)
$CoSO_4$	-30.9	5.06	5.08	5.21 (b)
$NiSO_4$	-82.0	3.45	3.52	3.82 (b)
$CuSO_4$	-55.0	1.94	1.93	1.91 (b)
$MnWO_4$	-53.6	5.67	5.75	5.44 (c)
$CoWO_4$	9.6	4.66	4.64	4.84 (c)
$NiWO_4$	-61.1	3.21	3.31	3.17 (c)
$CuWO_4$	18.0	1.67	1.67	1.49 (c)
$CoUO_4$	-	4.78	4.93	4.09 (d)

References (a) De Haas et al. (1940).

(b) Borovic-Romanov et al. (1957).

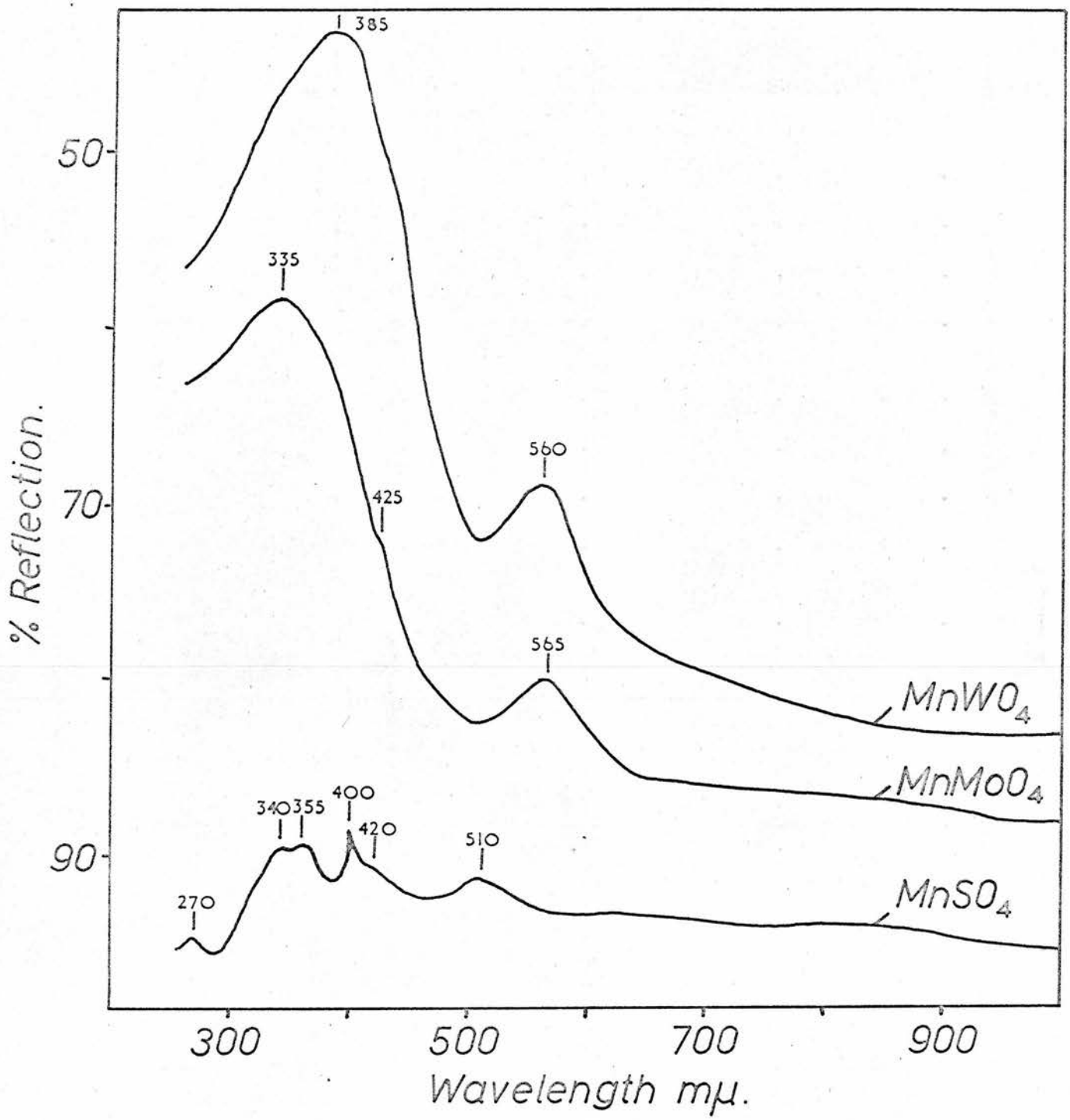
(c) Shapovalova et al. (1961).

(d) Bertaut et al. (1962).

tungstate there are very strong bands at 29,800 and 26,000 cm^{-1} respectively (figure 4) which can only be consistent with charge transfer. The spectrum of manganese (II) sulphate is interpreted in terms of the Orgel (1955, a) diagram by the method described by Orgel (1955, b). The degenerate states ^4E_g and $^4A_{1g}$, which are not affected by the field, occur at a separation 26,800 cm^{-1}

Figure 4.

Spectra of Manganese(II) Sulphate, Molybdate & Tungstate.



above the ground state in the free ion. The band at 25,000 cm^{-1} in manganese (II) sulphate is assigned to this transition; hence the ^6S - ^4G separation must be 1,800 cm^{-1} less in manganese (II) sulphate than in the free ion. All other ^4G levels are corrected by subtracting this factor, C_1 = 1,800 cm^{-1}, from the levels given on the Orgel diagram. As shown in table 3, predicted values, using a Dq value of 775 cm^{-1}, give good agreement with experimental data. The ^4E_g (D) state likewise is not affected by the field and a correction, C_2, can be applied to both ^4D levels in the same way. A correction for the ^4P level, which for the free ion lies between the ^4G and ^4D levels, is taken as the average of C_1 and C_2. The spectrum of manganese (II) molybdate can also be partly interpreted in this way although the transitions to all states above the ^4G states are obscured by the intense charge transfer band at 29,800 cm^{-1}. The band due to the transition to the $^4T_{2g}$ level, which is very weak in the spectrum of manganese (II) sulphate, is not observed in the molybdate or tungstate spectra. In the spectrum of manganese (II) tungstate, the transition to the ^4E_g, $^4A_{1g}$ level is not observed because of swamping by the very intense charge transfer band at 26,000 cm^{-1}, which is very close to the predicted value for this d-d transition. However, because of the similarity of the molybdate and tungstate spectra, the band at 17,700 cm^{-1} in manganese (II) tungstate can be assigned to the transition to the $^4T_{1g}$ level, and, assuming that the correction to be applied to the ^4G level is of the same

Table 3

State	$^4T_{1g}$	$^4T_{2g}$	$^4E_g, {}^4A_{1g}$	$^4T_{2g}$	^4E_g	$^4T_{1g}(P)$
$MnSO_4$						
Observed	19,600	23,800	25,000	28,200	29,400	37,000
Predicted, Dq = 775cm^{-1}	19,600	23,200	25,000	27,700	29,400	32,150
C cm^{-1}	C_1 = 1,800			C_2 2,900		C_3 2,350
$MnWO_4$						
Observed	17,850	-	Swamped by charge transfer band			
Predicted, Dq = 720cm^{-1}	17,850	21,750	23,500	at 26,000 cm^{-1}		
C cm^{-1}	C_1 3,300					
$MnMoO_4$						
Observed	17,700	-	23,500	Swamped by charge transfer band at 29,800 cm^{-1}		
Predicted, Dq = 730cm^{-1}	17,700	21,700	23,500			
C cm^{-1}	C_1 3,300					

order as for the molybdate, i.e. 3,300 cm^{-1}, a Dq value of 730 cm^{-1} gives agreement with the observed value.

For manganese (II), the magnetic moment is expected to be close to the spin-only value of 5.92 B.M., and the experimental moments of spin-free octahedral complexes lie in the range 5.65-6.10 B.M. [Figgis and Lewis, 1960]. The values obtained in the present work are slightly lower than this, which may indicate distortion from octahedral symmetry analogous to the slightly lower magnetic moments found in tetragonally distorted copper (II) complexes [Figgis and Harris, 1959].

The reflectance spectra for the cobalt salts (figure 5) are consistent with octahedrally coordinated cobalt (II) in a weak field. The bands are assigned as shown in table 4. The almost identical predicted transitions, made from the Orgel (1955, a) diagram and from the treatment of Ballhausen and Jørgensen (1955), give only qualitative agreement with the observed bands. The Dq value for cobalt (II) tungstate from the Orgel diagram, 700 cm^{-1}, is in good agreement with the previously reported value of 690 cm^{-1} [Ferguson et al., 1961]. For the molybdate, the band corresponding to the $^4T_{1g}$ to $^4A_{2g}$ transition is extremely weak and is observed only as a point of inflection. The $^4T_{1g}(F)$-$^4T_{1g}(P)$ band is known to split into two for some cobalt salts - Pratt and Coelho (1959) believe that this is due to tetragonal distortion. Presumably this, or a similar explanation holds for these salts.

Figure 5.
Spectra of Cobalt(II) Sulphate, Molybdate & Tungstate.

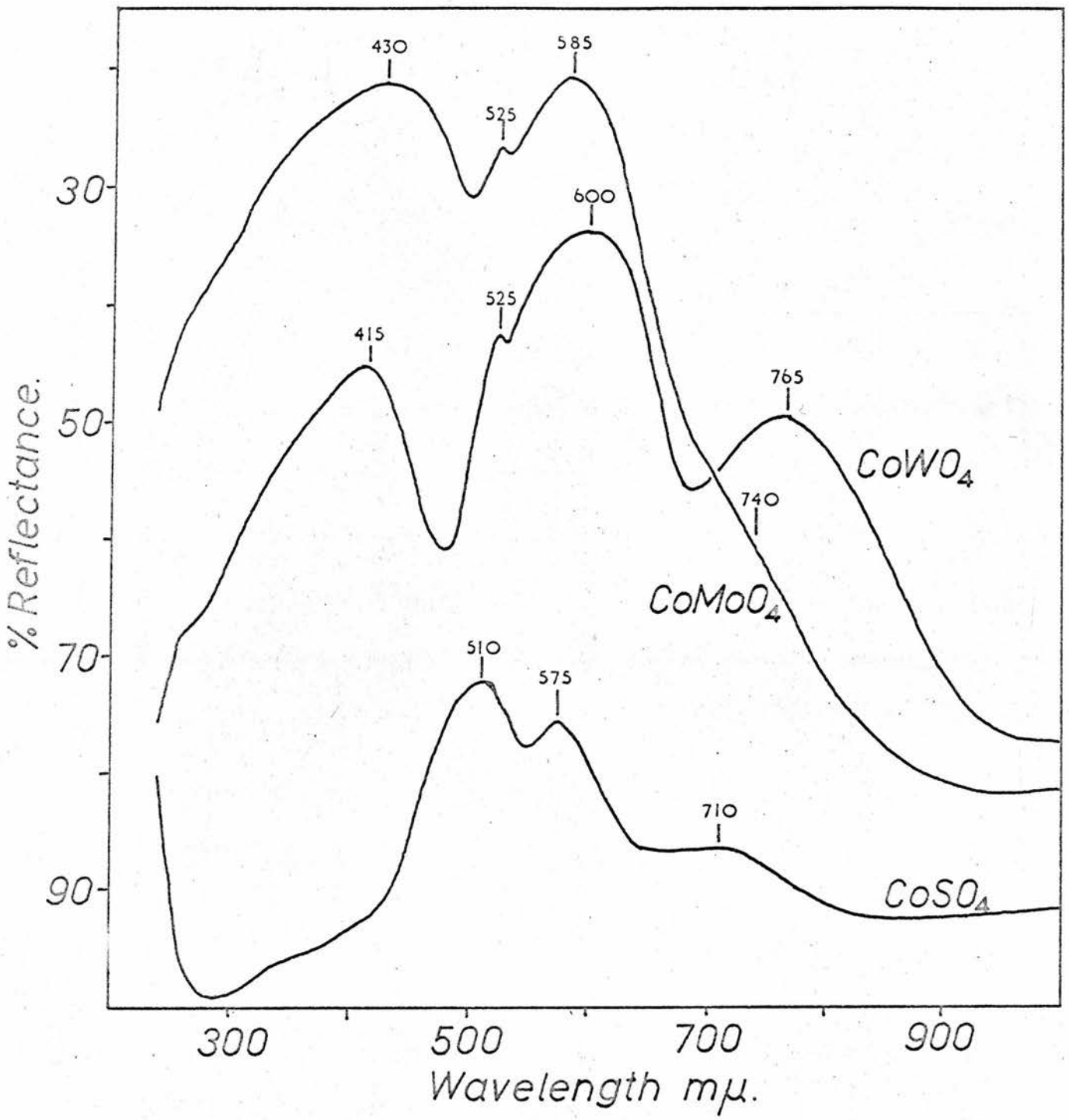


Table 4

State	$^4T_{2g}$	$^4A_{2g}$	$^4T_{1g}$	Charge Transfer
$CoSO_4$				
Observed	-	14,100	17,400 19,600	>44,500
Predicted (a) Dq = 750 cm^{-1}	6,640	14,100	20,600	
(b) Dq = 784 cm^{-1}	6,270	14,100	20,100	
$CoWO_4$				
Observed	-	13,100	16,700 19,050	24,100
Predicted (a) Dq = 700 cm^{-1}	6,130	13,100	19,900	
(b) Dq = 728 cm^{-1}	5,830	13,100	19,800	
$CoMoO_4$				
Observed	-	13,500	17,100 19,050	23,200
Predicted (a) Dq = 730 cm^{-1}	6,320	13,500	20,200	
(b) Dq = 751 cm^{-1}	6,010	13,500	19,900	

(a) Predicted from Orgel (1955) diagram.

(b) Predicted from the treatment of Ballhausen and Jørgensen (1955).

For spin-free cobalt (II), the effective magnetic moment is in the range 4.7-4.9 B.M. for octahedral coordination and in the range 4.2-4.4 B.M. for tetrahedral coordination [Figgis and Nyholm, 1959]. Cotton and Holm (1960) give the range for octahedral compounds of cobalt (II) as 4.8-5.3 B.M. and state that there is no evident correlation between the room temperature moment and the relative strength of the ligand field. The effective magnetic moments for the cobalt (II) compounds studied in the present work are in the range 4.7-5.3 B.M. thus supporting the proved octahedral coordination in the sulphate and tungstate and suggesting octahedral coordination in the molybdate.

The coordination of nickel (II) may be octahedral, tetrahedral or square planar. The spectra corresponding to each type of coordination are quite different and in most cases the difference is sufficient to distinguish between the three possible structures [Manch and Fernelius, 1961]. As shown in table 5 the spectra of nickel (II) sulphate (figure 6), molybdate and tungstate (figure 7) can be assigned on the basis of the Orgel (1955, a) diagram for the Ni^{2+} ion in an octahedral field. In the case of nickel (II) molybdate, the absorption at 20,600 and 23,500 cm^{-1} appear only as shoulders on the very intense charge transfer band at 28,600 cm^{-1}. This confirms the octahedral coordination of nickel (II) in the sulphate and tungstate and shows that in the molybdate also, nickel is octahedrally surrounded by oxygens.

Figure 6.
Spectra of Nickel(II) Sulphate.

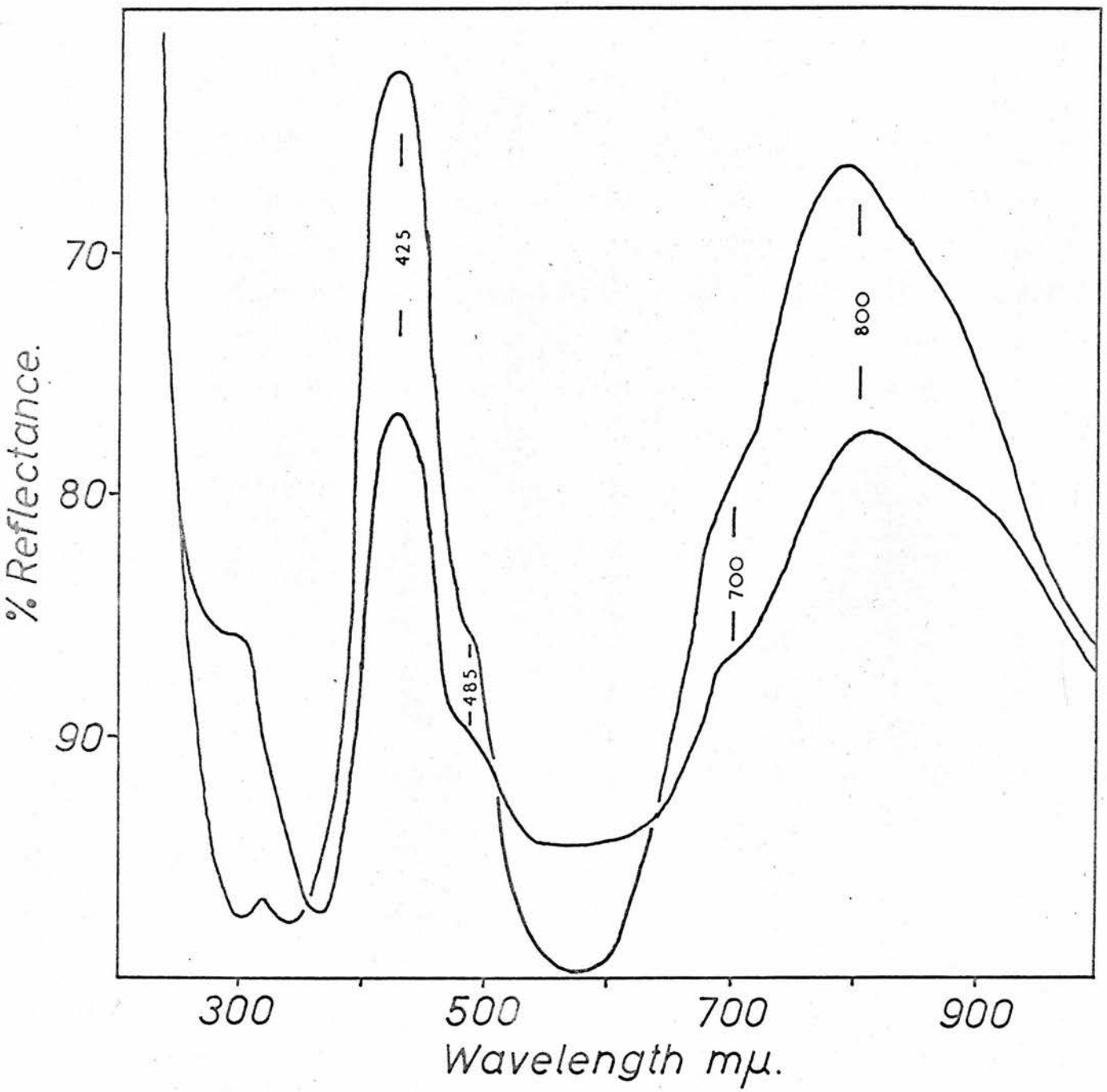


Figure 7.
Spectra of Nickel (II) Molybdate & Tungstate.

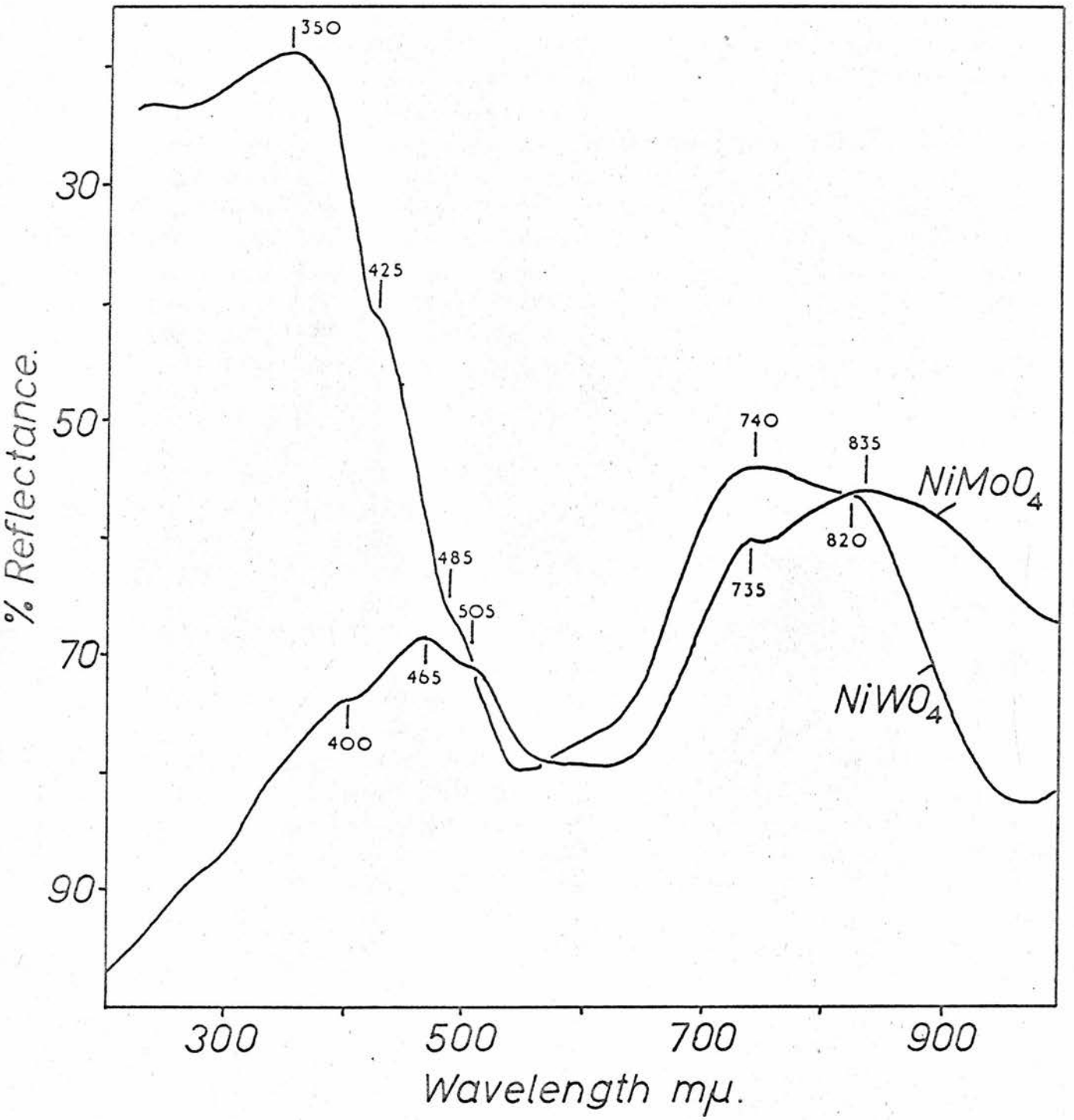


Table 5

State	$^3T_{2g}$	$^3T_{1g}(F)$	$^1E_{1g}$	$^1T_{2g}$	$^3T_{1g}(P)$	Charge transfer
$NiSO_4$						
Observed	-	12,500	14,300	20,600	23,500	>44,500
Predicted, Dq = 794 cm^{-1}	7,310	12,500	14,100	20,900	24,300	
$NiWO_4$						
Observed	-	12,000	13,600	19,800	21,500	25,000
Predicted, Dq = 755 cm^{-1}	6,750	12,000	13,900	20,600	23,800	
$NiMoO_4$						
Observed	-	12,200	13,500	20,600	23,500	28,600
Predicted, Dq = 760 cm^{-1}	6,820	12,200	13,950	20,750	23,900	

The moments normally found for octahedral nickel (II) compounds are in the range 3.0-3.3 B.M. [Miller, 1962], and thus the values for compounds studied in this work are consistent with octahedral coordination.

For copper (II), the effective magnetic moment is about 1.9 B.M. for compounds in which the coordination is octahedral or nearly so, and about 1.75 B.M. when there is tetragonal distortion from octahedral symmetry [Figgis and Harris, 1959]. The values for copper (II) tungstate - 1.73 B.M., and for copper (II) sulphate - 1.81 B.M., suggest distorted octahedral coordination for which there is X-ray evidence in the case of copper (II) sulphate [Kokkoros and Rentzeperis, 1958]. The value for copper (II) molybdate - 1.92 B.M. suggests that there is little distortion, but there is no apparent reason for this difference between the molybdate and tungstate.

The spectra of chromium (III) oxide, molybdate and tungstate are given in figures 9 and 10 and transitions predicted from the Orgel (1955, a) diagrams are given in table 6. There is little difference between the transitions predicted assuming tetrahedral or octahedral fields, there being only two absorption peaks which can be assigned to d-d transitions with any certainty. The Dq value required for an octahedral field is of the order expected, that is, about double that for divalent metal ions with the same ligands.

Figure 9
Spectra of Chromium(III) Oxide & Molybdate.

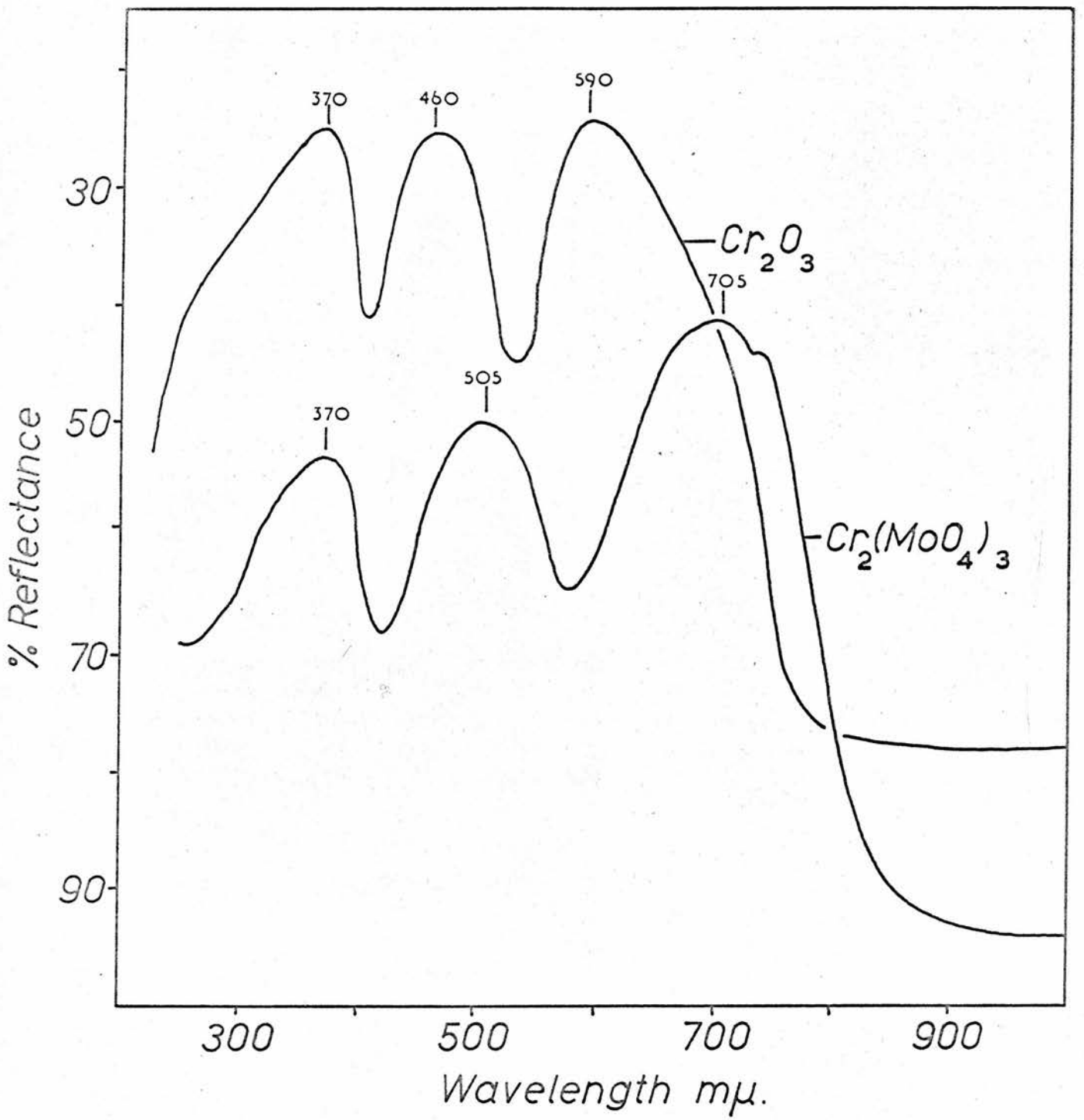


Figure 10.
Spectrum of Chromium(III) Tungstate.

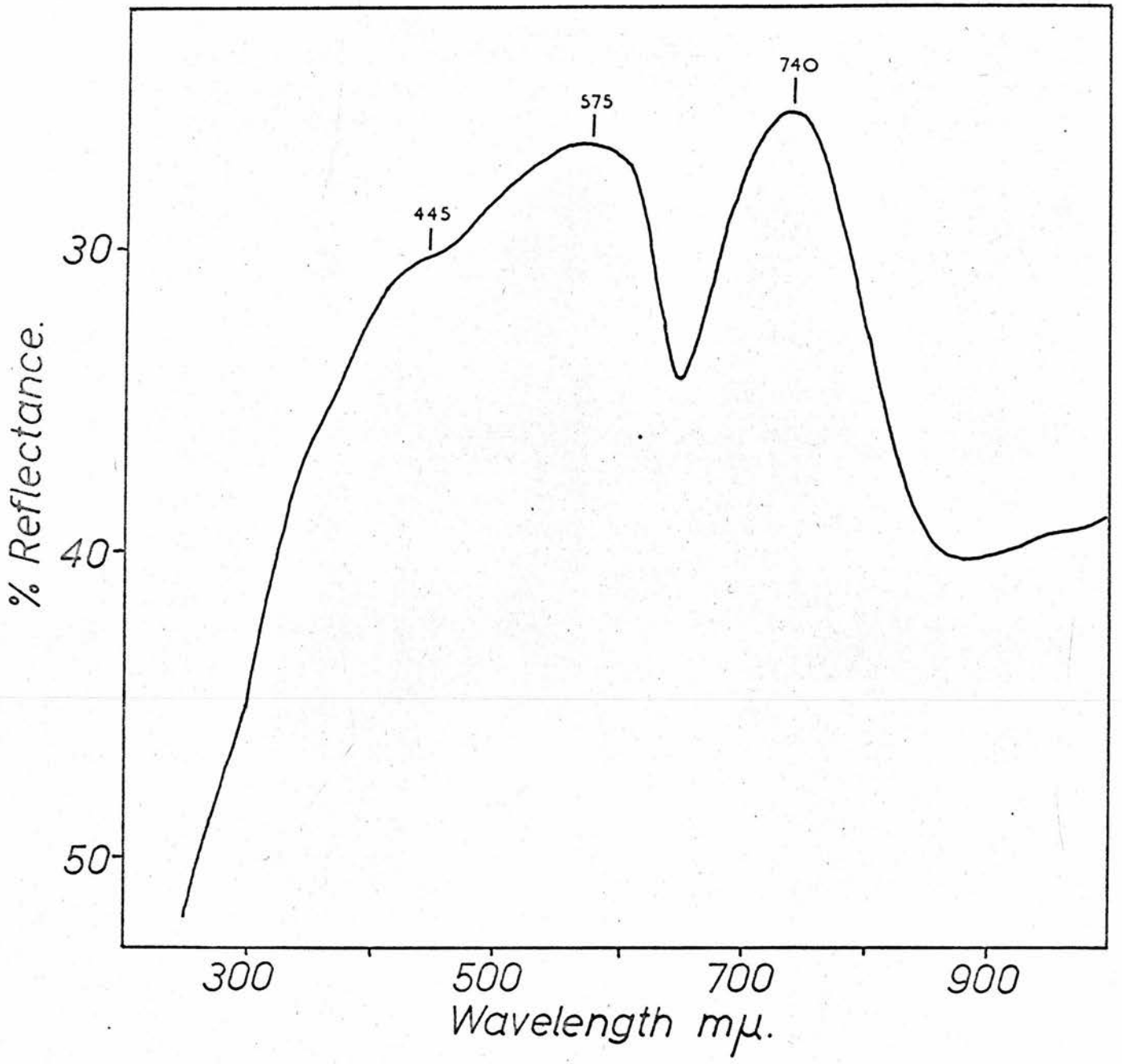
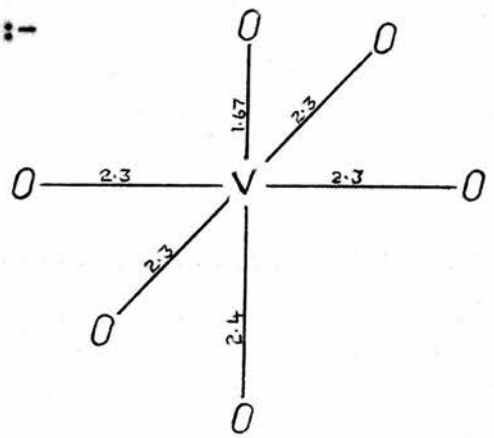


Table 6

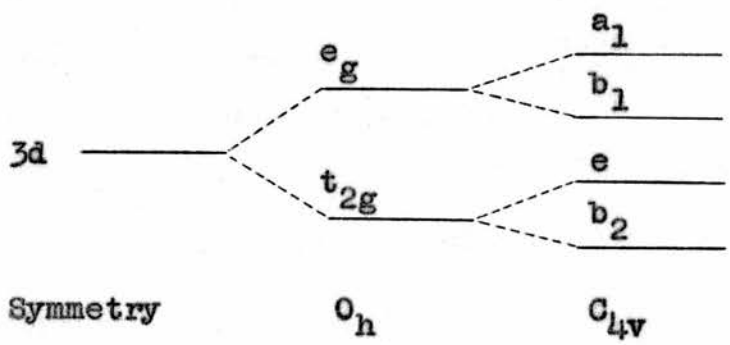
States	Tetrahedral Octahedral	$^4T_2$	$^4A_2$ $^4T_2$	$^4T_1(P)$ $^4T_1(F)$	Charge Transfer
Cr_2O_3	Observed		17,000	21,800	27,000
Tet.	Predicted, Dq = 830 cm^{-1}	8,200	17,000	20,800	
Oct.	Predicted, Dq = 1,700 cm^{-1}		17,000	25,500	
$Cr_2(MoO_4)_3$	Observed		14,200	19,800	27,000
Tet.	Predicted, Dq = 750 cm^{-1}	6,870	14,200	19,850	
Oct.	Predicted, Dq = 1,420 cm^{-1}		14,200	21,800	
Cr_2WO_6	Observed		13,500	17,400	22,500
Tet.	Predicted, Dq = 700 cm^{-1}	6,650	13,500	19,300	
Oct.	Predicted, Dq = 1,350 cm^{-1}		13,500	20,800	

The magnetic moment of both chromium (III) molybdate and tungstate, 3.43 and 3.01 B.M. respectively, is below that normally found for spin-free chromium (III) complexes - 3.70 to 3.90 B.M. [Figgis and Lewis, 1960]. The coordination of chromium (III) in these compounds cannot be deduced with any certainty from this magnetic and spectral study, using theoretical information available at present.

Ballhausen and Grey (1962) state that vanadyl complexes, containing the VO^{2+} ion, are five coordinate having the following spatial arrangement:-



this has C_{4V} symmetry which causes the 3d level to split as follows



Ballhausen and Grey (1962) have studied the spectra of several vanadyl complexes and have found bands corresponding to transitions

from the b_2 level as follows:-

1. at 12,600-13,100 cm^{-1} (b_2 -> c)
2. at 16,000-17,300 cm^{-1} (b_2 -> b_1)
3. at 25,300-29,400 cm^{-1} (b_2 -> a_1).

In addition, a strong charge transfer band at 41,700 cm^{-1} was found, which was stated to be characteristic of the VO^{2+} ion. In the spectrum of vanadyl molybdate, (figure 11), there is no evidence of a charge transfer band at 41,700 cm^{-1}. The observed absorption peaks do not occur in the positions predicted by Ballhausen and Grey (1962).

Vanadyl complexes usually have effective magnetic moments in the range 1.68-1.73 Bohr magnetons [Ballhausen and Grey, 1962]. In the case of vanadyl molybdate, the low value of 1.34 may be due to inadequate magnetic dilution, giving rise to magnetic interactions between neighbouring VO^{2+} ions.

The spectra of the uranates (figure 12) give no discrete features. They may be regarded as envelopes of the visible and charge transfer bands, which may be broadened by severe distortion of the field.

The effective magnetic moment of nickel (II) uranate is considerably lower than the other salts in the nickel series. The magnetic moment of both cobalt (II) and copper (II) uranates could both be taken to indicate octahedral coordination, but without supporting evidence from the spectra, no definite conclusions can be drawn as to the environment of the transition metal in these uranates.

Figure 11.
Spectrum of Vanadyl Molybdate.

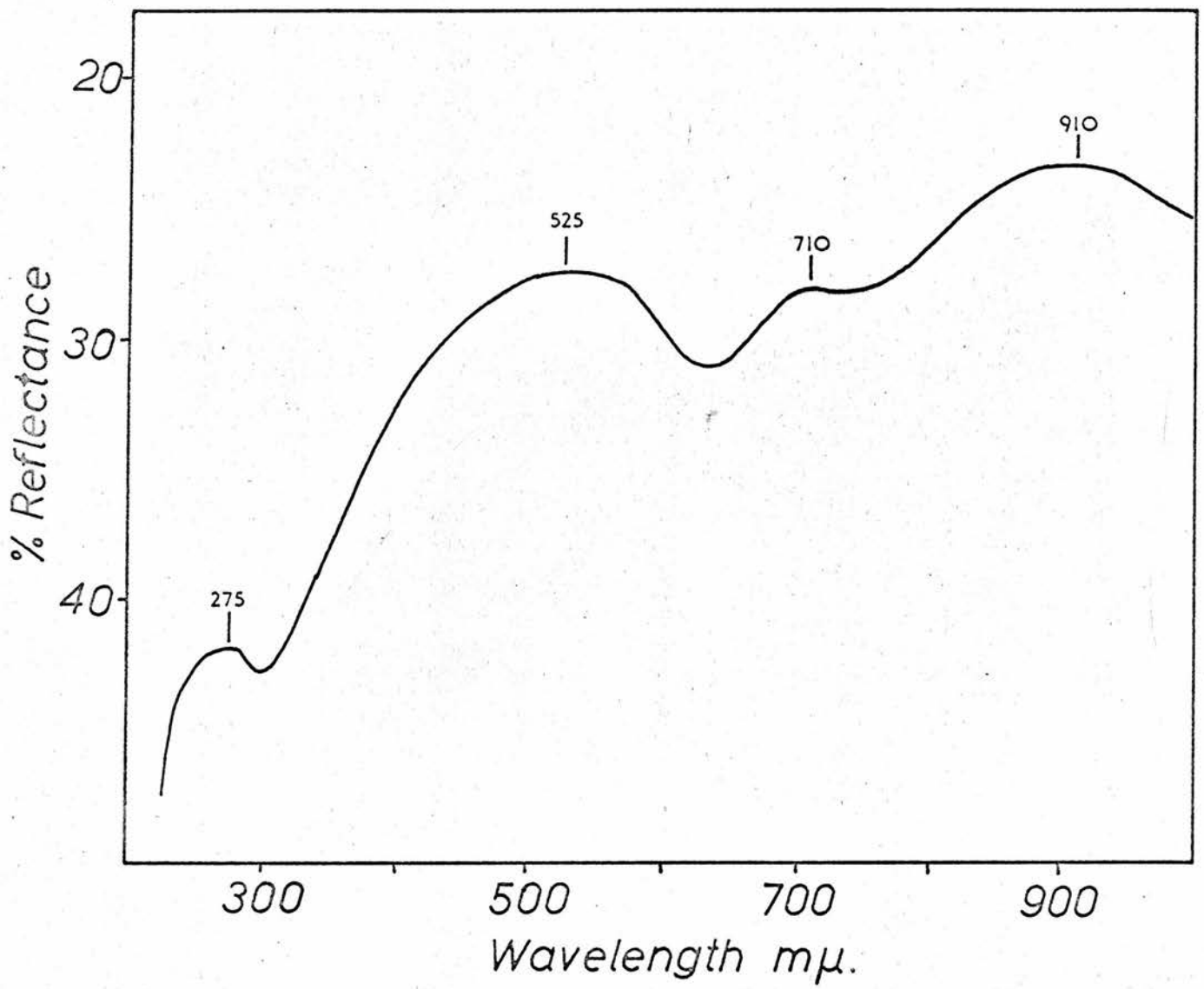
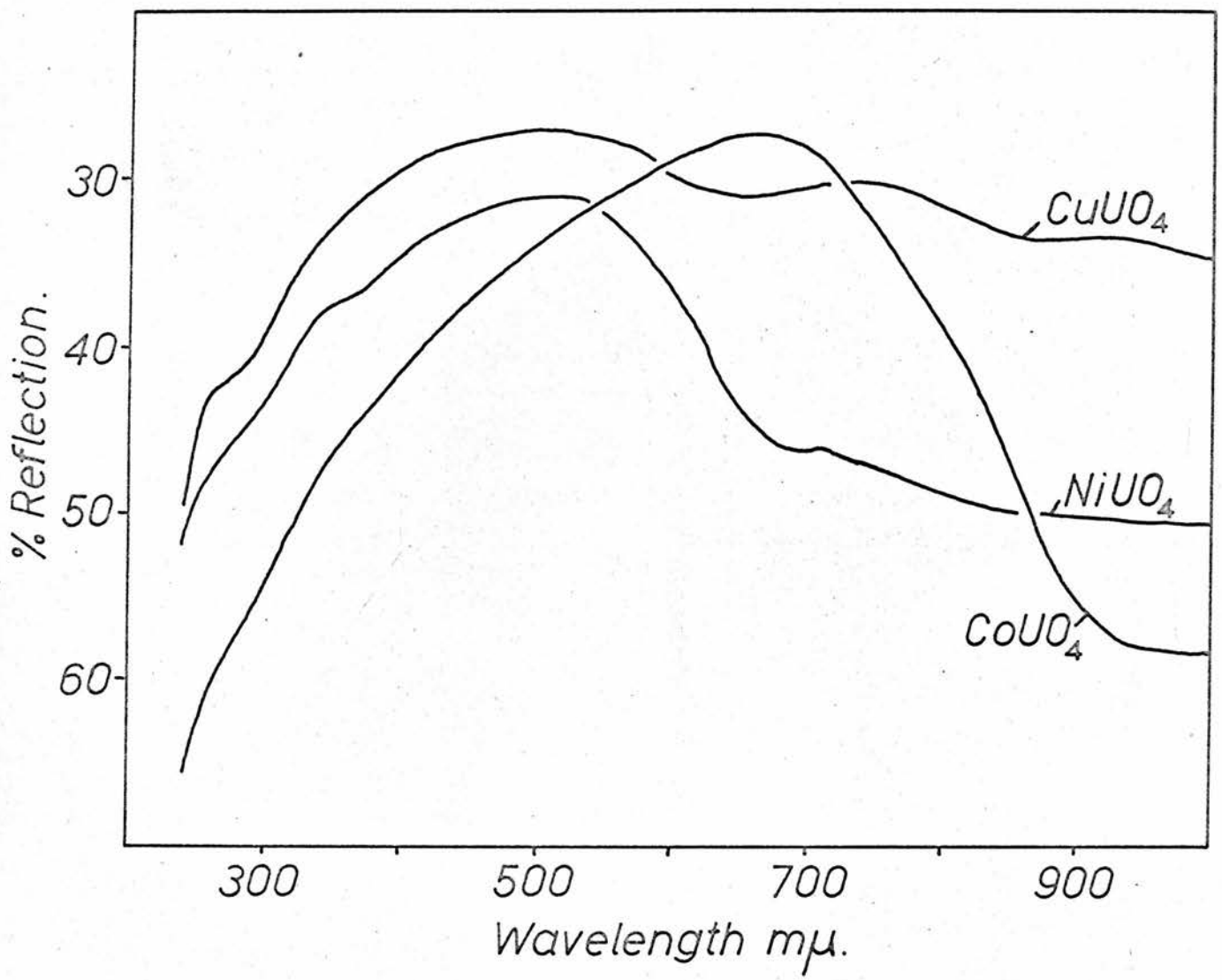


Figure 12.

Spectra of Cobalt(II), Nickel(II) & Copper(II) Uranates.



Conclusion

Six new molybdates of composition $Y_2O_3 \cdot 3MoO_3$, $Y_2O_3 \cdot 4MoO_3$, $HfO_2 \cdot 2MoO_3$, $V_2O_5 \cdot MoO_3$, $VO_2 \cdot MoO_3$ and $Cr_2O_3 \cdot 3MoO_3$ have been prepared at temperatures 660-700° C in the solid state and characterised by X-ray diffraction. Examination of these respective metal oxide-molybdenum (VI) oxide systems have shown these to be the only compounds formed under these conditions. Similar studies have proved the non existence of molybdates of titanium (II), (III) and (IV), vanadium (II) and (III) and niobium (IV) and (V).

The spectral and magnetic properties of the molybdates of manganese (II), cobalt (II), nickel (II) and copper (II) indicate that the transition metal ion is octahedrally coordinated by oxygen. The spectral and magnetic properties of chromium (III) molybdate, $Cr_2(MoO_4)_3$, and vanadyl molybdate, $VO.MoO_4$, give no conclusive evidence as to the coordination of the transition metal by oxygen.

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APPENDIX I

Effect of Field Strength on Susceptibility

Current (Amps)	10	8	6	4	2
Compound	10^6 X c.g.s. units				
$MnSO_4$	86.82	86.84	86.95	84.62	83.53
$MnMoO_4$	58.09	58.08	58.00	57.00	57.22
$MnWO_4$	38.20	38.19	37.95	37.25	37.72
$CoSO_4$	63.17	62.71	62.66	60.76	61.29
$CoMoO_4$	51.13	51.34	51.30	50.33	50.52
$CoWO_4$	31.22	31.23	31.12	30.48	30.52
$CoUO_4$	26.90	26.89	26.85	26.24	26.95
$NiSO_4$	25.60	25.57	25.57	25.56	24.60
$NiMoO_4$	18.50	18.52	18.43	18.22	17.73
$NiWO_4$	11.58	11.59	11.59	11.42	11.76
$NiUO_4$	6.03	6.04	6.10	6.20	6.48
$CuSO_4$	8.51	8.56	8.58	8.52	8.52
$CuMoO_4$	6.85	6.86	6.87	6.81	6.69
$CuWO_4$	3.98	4.01	4.02	3.98	3.94
$CuUO_4$	3.61	3.60	3.59	3.56	3.61
$Cr_2(MoO_4)_3$	17.02	17.00	16.98	16.65	16.96
Cr_2WO_6	19.99	19.97	19.83	19.32	19.68
$VO.MoO_4$	3.35	3.41	3.42	3.33	3.35

APPENDIX II

X-Ray d Spacings of the Oxides

Molybdenum (VI) oxide, MoO_3. Yellow

Source - commercial product heated at 600° C in air.

Diffractometer trace, 2θ = 2 to 44°.

Sample 1		Sample 2		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
6.97	100	6.92	75	6.93	34
3.82	21	3.80	30	3.81	82
3.47	100	3.47	100	3.463	61
3.26	11	3.26	21	3.260	100
3.01	3	3.02	5	3.006	13
2.706	2	2.706	3	2.702	19
2.659	3	2.652	6	2.655	35
2.607	1	2.607	2	2.607	6
2.529	1	2.535	3	2.527	12
				2.332	12
2.315	58	2.310	69	2.309	31
2.276	7	2.276	2	2.271	18
2.131	1	2.131	3	2.131	9

Reference - Swanson, N.B.S. Circular 539, 3, (1953)

A.S.T.M., 5-0508.

Molybdenum (IV) oxide, MoO_2. Purple

Source - reduction of molybdenum (VI) oxide by hydrogen at 400° C.

Diffractometer trace, 2θ = 2 to 58°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.82	4	4.78	20
3.44	100	3.41	100
2.823	3	2.804	30
2.436	53	2.433	50
		2.420	85
2.411	48	2.405	40
		2.397	50
2.186	4	2.176	30
		2.171	10
2.161	5	2.147	30
1.841	5	1.833	35
1.725	20	1.718	55
1.713	33	1.704	80
1.701	22	1.692	50

Reference - Magneli, Uppsala Univ., Sweden.

A.S.T.M., 5-0452.

Tungsten (VI) oxide, WO_3. Green

Source - commercial product heated at 1000° C in air.

Diffractometer trace, 2θ = 2 to 43°.

2°/min.		½°/min.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.85	81	3.85	88	3.835	100
3.78	64	3.77	56	3.762	95
3.66	100	3.66	100	3.642	100
3.36	8	3.36	4	3.411	5
		3.32	2	3.342	50
3.13	4	3.12	5	3.109	50
3.09	14	3.10	15	3.076	50
2.722	8	2.714	6		
2.698	14	2.698	9	2.684	75
2.675	26	2.667	15	2.661	60
2.629	36	2.629	22	2.617	90
		2.607	7		
2.542	1	2.529	1	2.528	35
2.515	2	2.515	2	2.509	40
2.176	3	2.181	2	2.172	50
2.156	12	2.156	9	2.149	60

Reference - Magneli, Uppsala Univ., Sweden.

A.S.T.M., 5-0363.

Triuranium octoxide, U_3O_8. Brown

Source - commercial uranium (VI) oxide heated to 1000° C in air.

Diffractometer trace, 2θ = 2 to 47°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
		5.87	10
4.17	100	4.15	100
3.43	41	3.43	100
3.36	24	3.36	50
2.644	38	2.64	90
2.614	24	2.61	40
2.217	1		
2.083	24	2.07	40
1.994	5	1.99	20
1.953	11	1.95	40

Reference - A.S.T.M., 2-0276.

Yttrium (III) oxide, Y_2O_3. White

Source - commercial product heated at 660° C in air.

Diffractometer trace, 2θ = 10 to 37°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.33	17	4.34	16
3.07	100	3.060	100
2.659	24	2.652	30
2.502	5	2.500	7

Reference - Swanson, N.B.S. Circular 539, 3, (1953)

A.S.T.M., 5-0574.

Titanium (IV) oxide, TiO_2 (Anatase). White

Source - commercial product heated to 700° C in air.

Diffractometer trace, 2θ = 2 to 50°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.51	100	3.51	100
2.436	5	2.435	9
2.380	16	2.379	22
2.338	5	2.336	9
1.891	20	1.891	33

Reference - Swanson, J.C. Fel. Reports, N.B.S., (1950)

A.S.T.M., 4-0477.

Titanium (III) oxide, Ti_2O_3. Purple

Source - reduction of titanium (IV) oxide with titanium metal at 1,200° C in argon.

Diffractometer trace, 2θ = 2 to 45° and powder photograph.

		Photo.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.75	94	3.78	25		
3.56	34	3.58	10		
2.722	100	2.73	100	2.68	50
2.578	77	2.59	75	2.52	50
2.243	34	2.276	75	2.21	20
2.191	11				
2.108	11				

Reference - Halla, Z. anorg. Chem., 184, 423 (1929).

A.S.T.M., 2-1359.

Titanium (II) oxide, TiO. Silver grey

Source - reduction of titanium (IV) oxide by titanium metal at 1,200° C in argon.

Powder photograph.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
2.40	50	2.407	45
2.07	100	2.085	100
1.466	100	1.475	50
1.251	40	1.259	13
1.199	40	1.205	12
0.952	25	1.044	5

Reference - Paretzkin, Polytechnic Inst. Brooklyn.
A.S.T.M., 8-117.

Hafnium (IV) oxide, HfO_2. White

Source - spectroscopically pure commercial product.

Diffractometer trace, 2θ = 5 to 40°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
5.13	7	5.07	20
3.69	21	3.68	40
3.62	21	3.61	30
3.16	100	3.15	100
2.832	77	2.82	100
2.600	38	2.59	60
2.535	32	2.52	50
2.502	5	2.48	20
2.321	10	2.32	50

Reference - Geller, Analyt. Chem., 25, 1774 (1953).

A.S.T.M., 6-0318.

Vanadium (V) oxide, V_2O_5. Orange

Source - commercial product heated at 600° C in air.

Diffractometer trace, 2θ = 25 to 41°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.41	100	3.40	90
2.876	75	2.88	65
2.754	38	2.76	35
		2.687	15
2.607	33	2.610	40

Reference - Swanson, N.B.S. Circular 539, 8, (1958).

A.S.T.M., 9-387.

Vanadium (IV) oxide, VO_2. Brown

Source - vanadium (III) oxide and vanadium (V) oxide reacted at 1,000° C in nitrogen.

Diffractometer trace, 2θ = 5 to 39°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.53	7		
3.35	23	3.31	30
3.23	100	3.20	100
3.10	4		
2.979	5	2.68	30
2.436	27	2.430	40

Reference - Andersson, Acta Chem. Scand., 8, 1599 (1954).

A.S.T.M., 9-142.

Vanadium (III) oxide, V_2O_3. Black

Source - reduction of vanadium (V) oxide by hydrogen at 900° C.

Diffractometer trace, 2θ = 2θ to 48°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.65	75	3.65	60
2.706	100	2.70	80
2.475	79	2.47	60
		2.32	2
2.186	37	2.18	20

Reference - Hanawalt, Analyt. Chem., 10, 457 (1938).

A.S.T.M., 1-1293.

Vanadium (II) oxide, VO. Black (Impure)

Source - reduction of vanadium (V) oxide by vanadium metal at 1,300° C in hydrogen.

Diffractometer trace, 2θ = 10 to 50°.

		Reference		V_2O_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.66	21			3.65	75
2.706	36			2.706	100
2.488	26			2.475	79
2.374	67	2.355	S		
2.191	13			2.186	37
2.054	100	2.050	VS		

Reference - Mathewson, Trans. Amer. Soc. Steel Testing, 20, 361 (1932).

Niobium (V) oxide, Nb_2O_5. White

Source - commercial product heated at 650° C in air.

Diffractometer trace, 2θ = 12 to 29°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
5.13	19	5.13	20
		4.74	<10
4.65	8	4.63	20
		3.83	<10
		3.75	70
3.75	100	3.74	50
3.66	53	3.65	100
3.59	58	3.56	<10
3.51	56	3.49	50
		3.41	<10
3.36	14	3.36	10
		3.32	<10

Reference - Holtzberg, J. Amer. Chem. Soc., 79, 2039 (1957).

A.S.T.M., 9-372.

Niobium (V) oxide, Nb_2O_5. White

Source - oxidation of niobium (IV) oxide by heating in air at 650° C.

Diffractometer trace, 2θ = 15 to 52°.

Sample 1		Sample 2		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.93	100	3.95	100	3.925	90
3.15	58	3.15	58	3.124	100
3.09	30	3.10	33		
2.455	20	2.461	23	2.446	40
2.430	14	2.436	16		
1.965	12	1.969	15	1.962	30
1.827	4	1.831	6		
1.791	7	1.797	6	1.800	25

Reference - Frevel, Analyt. Chem., 27, 1329 (1955).

A.S.T.M., 7-61.

Niobium (IV) oxide, NbO_2. Black

Source - reduction of niobium (V) oxide with hydrogen at 1,125° C.

Diffractometer trace, 2θ = 12 to 45°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.63	3	3.63	30
3.43	100	3.42	100
3.21	5	3.21	30
		2.91	30
2.542	67	2.54	80
2.495	3	2.491	30
2.423	18	2.422	50
		2.341	20
2.249	9	2.253	30

Reference - Magneli, Acta Chem. Scand., 9, 1402 (1955).

A.S.T.M., 9-235.

Chromium (III) oxide, Cr_2O_3. Green

Source - commercial product heated at 1,000° C in air.

Diffractometer trace, 2θ = 2 to 45°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
3.65	61	3.633	74
2.683	100	2.666	100
2.488	52	2.480	96
2.281	36	2.264	12
2.186	24	2.176	38

Reference - Swanson, N.B.S. Circular 539, 5, (1955).

A.S.T.M., 6-0504.

Manganese (II) oxide, MnO. Grey

Source - decomposition of manganese (II) carbonate in nitrogen at 600° C.

Diffractometer trace, 2θ = 10 to 58°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
2.571	56	2.568	62
2.227	100	2.223	100

Reference - Swanson, N.B.S. Circular 539, 5, 45 (1955).

A.S.T.M., 7-230.

Cobalt (II) oxide, CoO. Brown

Source - decomposition of cobalt (II) carbonate at 1,000° C in nitrogen.

Diffractometer trace, 2θ = 2 to 47°, and powder photograph.

		Photo.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
2.461	86	2.45	70	2.460	75
2.131	100	2.127	100	2.130	100
		1.503	100	1.5062	50
		1.279	70	1.2846	20
		1.224	50	1.2298	15
				1.0651	9
		0.974	30	0.9775	13
		0.950	30	0.9526	30

Reference - Swanson, N.B.S. Circular 539, 9, (1959).
A.S.T.M., 9-402.

Nickel (II) oxide, NiO. Green

Source - decomposition of AnalaR nickel (II) nitrate hexahydrate and ignition at 950° C in air.

Diffractometer trace, 2θ = 2 to 86°, and powder photograph.

		Photo.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
2.417	58	2.340	90	2.410	91
2.094	100	2.035	100	2.088	100
1.478	21	1.456	100	1.476	57
1.259	8	1.246	75	1.259	16
1.205	6	1.194	75	1.206	13
		1.038	50	1.0441	8

Reference - Swanson, J.C. Fel. Reports, N.B.S., (1950).
A.S.T.M., 4-0835.

Copper (II) oxide, CuO. Black

Source - commercial product heated at 1,000° C in air.

Diffractometer trace, 2θ = 2 to 55°.

2°/min.		½°/min.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		2.754	10	2.751	12
				2.530	49
2.535	100	2.529	100	2.523	100
2.327	75	2.327	84	2.323	96
				2.312	30
				1.959	3
1.873	16	1.866	13	1.866	25
				1.788	2
		1.713	5	1.714	8

Reference - Swanson, N.B.S. Circular 539, 1, 49 (1953).

A.S.T.M., 5-0661.

APPENDIX III

X-Ray d Spacings of the Molybdates

Yttrium (III) molybdate, $Y_2O_3.3MoO_3$. White

Source - reaction of yttrium (III) oxide with molybdenum (VI) oxide at 660° C in air.

Diffractometer trace, 2θ = 2 to 40°, at $\frac{1}{2}$°/min..

dÅ	I/I_o	(continued)	
		dÅ	I/I_o
10.52	14		
5.99	11	3.18	5
5.28	32	3.12	15
5.16	14	3.01	60
4.65	76	2.912	38
4.29	12	2.780	27
3.69	100	2.578	16
3.65	52	2.398	5
3.52	55	3.368	5
3.45	100	2.356	3
3.26	66	2.310	16

Yttrium (III) molybdate, $Y_2O_3.4MoO_3$. White

Source - reaction of yttrium (III) oxide with molybdenum (VI) oxide at 660° C in air.

Diffractometer trace, 2θ = 2 to 40°, at $\frac{1}{2}$°/Min..

dÅ	I/I_o
6.97	26
6.56	12
4.48	32
4.40	35
4.33	15
4.19	40
3.87	29
3.82	3
3.57	47
3.48	100
3.44	36
3.35	43
3.21	24

(continued)

dÅ	I/I_o
3.18	29
3.11	29
3.02	2
2.876	22
2.780	14
2.706	17
2.614	21
2.392	7
2.327	11
2.310	10
2.254	7

The yttrium (III) oxide - molybdenum (VI) oxide system at 660° C.

Y_2O_3		1:2.5		1:3.0		1:3.2	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
						4.40	15
4.33	17	4.29	12	4.29	12	4.29	7
						4.19	22
						3.87	13
		3.71	100	3.69	100	3.69	87
		3.66	64	3.65	52	3.65	58
						3.57	20
		3.53	59	3.52	55	3.52	48
						3.49	50
		3.47	97	3.45	100	3.45	100
						3.35	2
		3.26	63	3.26	66	3.26	54
						3.21	11
				3.18	5	3.18	17
		3.13	14	3.12	15	3.11	17
3.07	100	3.07	22				
		3.01	56	3.01	60	3.01	50
		2.912	44	2.912	38	2.912	33
						2.867	11
		2.788	27	2.780	27	2.780	33
						2.706	11
2.659	24	2.644	5				

Diffractometer traces, 2θ = 20 to 34°.

1:3.9		1:4.0		1:4.5		1:5.0		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
4.40	43	4.40	35	4.40	26	4.37	29		
4.33	19	4.33	15	4.35	12	4.33	16		
4.19	43	4.19	40	4.19	11	4.19	28		
3.88	32	3.87	29	3.87	9	3.87	20		
		3.82	3	3.80	3	3.80	13	3.82	21
3.71	6								
3.65	5								
3.59	53	3.57	47	3.59	21	3.57	34		
3.49	100	3.48	100	3.49	100	3.48	100		
						3.47	59	3.47	100
3.45	30								
		3.44	36	3.45	12	3.44	18		
3.35	45	3.35	43	3.33	15	3.33	27		
						3.26	5	3.26	11
3.22	26	3.21	24	3.20	8	3.20	17		
3.19	40	3.18	29	3.18	10	3.18	22		
3.11	36	3.11	29	3.11	12	3.10	20		
3.01	4	3.02	2						
2.876	19	2.876	22	2.867	7	2.867	17		
2.780	19	2.780	14	2.771	7	2.771	12		
2.706	19	2.706	17	2.698	6	2.698	13		

Titanium (IV) oxide - molybdenum (VI) oxide reaction product

Source - materials heated at 700° C in air.

Diffractometer trace, 2θ = 20 to 40°.

Ratio 2:1		Ratio 1:2		MoO_3		Anatase		Rutile (Ref.)	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.85	18	3.83	16	3.82	21				
3.55	44					3.51	100		
3.49	100	3.49	100	3.47	100				
3.29	14	3.26	6	3.26	11			3.245	100
		3.02	2	3.01	3				
2.502	16	2.509	9					2.489	41
2.392	6					2.380	16		
2.321	42	2.315	53	2.315	58				
2.281	5	2.276	6	2.276	7				

Reference - Swanson, J.C. Fel. Reports, N.B.S. (1950).

A.S.T.M., 4-0551.

Titanium (III) oxide - molybdenum (VI) oxide reaction product

Source - 1:1 mixture heated at 700° C in argon.

Diffractometer trace, 2θ = 25 to 42°.

		MoO_2		Anatase		Rutile (Ref.)	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.52	5			3.51	100		
3.43	100	3.44	100				
3.25	23					3.245	100
2.488	11					2.489	41
2.436	44	2.436	53	2.436	5		
2.417	20	2.411	48	2.380	16		
2.191	10					2.188	22

Reference - Swanson, J.C. Fel. Reports, N.B.S. (1950).

A.S.T.M., 4-0551.

Titanium (II) oxide - molybdenum (VI) oxide reaction product

Source - 2:1 mixture heated at 650° C in nitrogen.

Diffractometer trace, 2θ = 25 to 40°.

		MoO_2		Rutile (Reference)	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.44	100	3.44	100		
3.25	15			3.245	100
2.495	6			2.489	41
2.430	33	2.436	53		
2.411	29	2.411	48		

Reference - Swanson, J.C. Fel. Reports, N.B.S. (1950).

A.S.T.M., 4-0551.

Hafnium Molybdate, $HfO_2 \cdot 2MoO_3$. White

Source - reaction of hafnium (IV) oxide with molybdenum (VI) oxide at 700° C in air.

Diffractometer trace, 2θ = 2 to 65°.

		$ZrO_2 \cdot 2MoO_3$	
dÅ	I/I_o	dÅ	I/I_o
5.95	83	5.79	16
5.10	3		
3.85	100	3.85	100
2.931	22	2.941	46
2.621	1		
2.542	32	2.542	23
2.327	7	2.333	5
1.961	14	1.957	10
1.918	11	1.922	9
1.810	11	1.824	15
1.689	3	1.695	3
1.626	7	1.626	6
1.603	4	1.603	2
1.465	2	1.465	3

The hafnium (IV) oxide - molybdenum (VI) oxide system at 700° C.
Diffractometer traces, 2θ = 12 to 40°.

HfO_2		1:1		1:2		1:2.76		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
						6.92	4	6.97	100
		5.87	8	5.95	83	5.91	20		
5.13	7								
		5.07	6	5.10	3	5.07	4		
		3.83	100	3.85	100	3.85	100	3.82	21
3.69	21	3.66	2						
3.62	21	3.62	2						
						3.47	8	3.47	100
						3.26	3	3.26	11
3.16	100	3.14	15						
		2.912	41	2.931	22	2.922	32		
2.832	77	2.832	11						
		2.614	5	2.621	1				
2.600	38	2.593	5						
2.535	32	2.535	23	2.542	32	2.542	35		
		2.321	14	2.327	7	2.327	15		

Vanadium (V) molybdate, $V_2O_5 \cdot MoO_3$. Brown

Source - reaction of vanadium (V) oxide with molybdenum (VI) oxide at 640° C in air.

Diffractometer trace, 2θ = 2 to 36°.

dÅ	I/I_o
9.83	2
5.87	1
4.90	3
4.60	1
4.33	8
4.15	100
3.82	2

(continued)

dÅ	I/I_o
3.57	5
3.24	4
3.13	2
2.706	2
2.659	1
2.564	1

The vanadium (V) oxide - molybdenum (VI) oxide system at 640° C.
Diffractometer traces, 2θ = 24 to 40°.

V_2O_5		1.2:1		1:1		1:1.2		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		3.57	100	3.57	90	3.57	72		
						3.47	14	3.47	100
3.41	100	3.44	38						
		3.23	100	3.24	100	3.23	100		
		3.13	50	3.13	43	3.12	24		
2.876	75	2.894	53						
2.754	38	2.763	28						
		2.706	43	2.706	38	2.698	24		
		2.644	35	2.659	33	2.644	21		
		2.556	13	2.564	19	2.556	14		
						2.315	10	2.315	58

Vanadium (IV) molybdate, $VO(MoO_4)$. Brown

Source - reaction of vanadium (IV) oxide with molybdenum (VI) oxide at 700° C in nitrogen.

Diffractometer trace, 2θ = 2 to 30°.

dÅ	I/I_o
6.11	3
4.69	6
4.55	2
4.29	100
4.04	9

(continued)

dÅ	I/I_o
3.60	26
3.31	39
3.16	69
3.05	2

The vanadium (IV) oxide - molybdenum (VI) oxide system at 700° C.

Diffractometer traces, 2θ = 24 to 30°.

VO_2		1.22:1		1:1		0.95:1		0.51:1		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		3.60	37	3.60	33	3.60	39	3.60	29		
3.53	7	3.56	5								
						3.48	5	3.47	62	3.47	100
3.35	23	3.31	50	3.31	49	3.31	63	3.31	74		
								3.27	43	3.26	11
3.23	100	3.22	2								
		3.16	100	3.16	100	3.16	100	3.16	100		
		3.05	2	3.05	3	3.05	3	3.02	11		

Vanadium (III) oxide - molybdenum (VI) oxide reaction product

Source - 1:1 mixture heated at 700° C in nitrogen.

Diffractometer trace, 2θ = 2 to 43°.

		MoO_2	
dÅ	I/I_o	dÅ	I/I_o
3.30	100	3.44	100
2.442	49	2.436	53
2.333	6	2.411	48
2.166	8	2.161	5

Vanadium (II) oxide - molybdenum (VI) oxide reaction product

Source - mixture reacted at 700° C in nitrogen.

Diffractometer trace, 2θ = 10 to 50°.

		V_2O_3	
dÅ	I/I_o	dÅ	I/I_o
3.63	74	3.65	75
2.714	100	2.706	100
2.475	81	2.475	79
2.186	39	2.186	37

The niobium (V) oxide - molybdenum (VI) oxide system

Source - mixtures heated at 660° C in air.

Diffractometer traces, 2θ = 23 to 30°.

Nb_2O_5		4:1		1:1		1:2		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
						3.88	30		
				3.85	4				
						3.82	11	3.82	21
3.75	100	3.75	72	3.75	39	3.75	22		
3.66	53								
		3.60	100	3.60	100	3.63	100		
3.59	58								
3.51	56	3.52	88						
				3.47	7	3.47	52	3.47	100
3.36	14	3.35	9						
						3.29	15	3.26	11

Niobium (IV) oxide - molybdenum (VI) oxide reaction product

Source - 2:1 mixture heated at 660° C in nitrogen.

Diffractometer trace, 2θ = 2 to 55°.

		Nb_2O_5		MoO_2	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
3.93	100	3.93	100		
3.43	73			3.44	100
3.14	53	3.15	58		
3.08	24	3.09	30		
2.455	27	2.455	20		
				2.436	53
2.430	33	2.430	14		
				2.411	48
1.969	14	1.965	12		
1.827	5	1.827	4		
1.791	7	1.791	7		
1.725	9			1.725	20
1.713	16			1.713	33
1.698	7			1.701	22

Chromium (III) molybdate, $Cr_2(MoO_4)_3$. Violet

Source - reaction of chromium (III) oxide with molybdenum (VI) oxide at 660° C in air.

Diffractometer trace, 2θ = 2 to 35°, at $\frac{1}{2}$°/min..

dÅ	I/I_o
6.38	25
5.75	23
4.53	10
4.31	32
4.07	33
3.88	38
3.83	100
3.72	13
3.55	27
3.44	49

(continued)

dÅ	I/I_o
3.32	7
3.23	31
3.19	29
3.12	7
2.941	23
2.876	8
2.823	14
2.637	8
2.614	23

The chromium (III) oxide - molybdenum (VI) oxide system at 660° C.

Diffractometer traces, 2θ = 21 to 40°.

Cr_2O_3		70%MoO_3		73%MoO_3		77%MoO_3		80%MoO_3		MoO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		4.06	37	4.08	53	4.08	32	4.10	29		
		3.90	35	3.88	48	3.90	33	3.92	34		
		3.85	100	3.85	100	3.85	100	3.87	95		
								3.82	26	3.82	21
		3.72	12	3.72	13	3.72	10	3.75	10		
3.65	61	3.63	4	3.63	4						
		3.55	25	3.55	27	3.55	24	3.57	22		
						3.47	13	3.48	100	3.47	100
		3.44	44	3.45	57	3.44	60	3.44	24		
		3.32	6	3.32	8	3.33	5				
								3.29	10		
										3.26	11
		3.23	27	3.23	40	3.23	27	3.24	26		
		3.19	33	3.19	20	3.19	33	3.20	29		
		3.12	10	3.12	9	3.13	9	3.13	3		
		2.941	19	2.950	29	2.941	21	2.960	21		
		2.876	10	2.876	10	2.876	9	2.894	5		
		2.823	13	2.832	20	2.823	11	2.841	10		
2.683	100	2.667	6	2.644	9						
		2.614	17	2.614	26	2.614	21	2.629	19		
2.488	52	2.475	6								
		2.374	8	2.380	10	2.380	10	2.380	3		
						2.310	13	2.321	40	2.315	58

Manganese (II) molybdate, $MnMoO_4$. Buff

Source - reaction of manganese (II) oxide with molybdenum (VI) oxide in nitrogen.

Diffractometer trace, 2θ = 10 to 40°.

		MoO_3	
dÅ	I/I_o	dÅ	I/I_o
6.97	10	6.97	100
4.74	10		
3.92	26	3.82	21
3.60	20		
3.47	100	3.47	100
3.33	31		
3.30	11	3.26	11
3.22	26		
2.867	20		
2.788	8		
2.714	23		
2.529	8		
2.386	16		
2.310	21	2.315	58

The manganese (II) oxide - molybdenum (VI) oxide system at 700° C.

Diffractometer traces, 2θ = 22 to 41°.

MnO		1.7:1		1.45:1		1:1		1:1.12		MoO_3	
dÅ	I/I_o	dÅ	I/I_c	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		3.92	17	3.92	20	3.92	26	3.92	13		
								3.83	8	3.82	21
		3.62	8	3.62	13	3.60	20	3.62	9		
		3.47	100	3.47	100	3.47	100	3.47	100	3.47	100
		3.33	21	3.33	22	3.33	31	3.35	20		
				3.29	13	3.30	11	3.27	8		
										3.26	11
		3.22	15	3.22	13	3.22	26	3.22	14		
		2.867	15	2.857	15	2.867	20	2.867	15		
		2.780	6	2.788	8	2.788	8	2.788	5		
		2.714	23	2.714	20	2.714	23	2.714	21		
2.571	56	2.571	17	2.571	10						
		2.515	12	2.522	11	2.529	8	2.522	8		
		2.374	8	2.386	9	2.386	16	2.386	6		
		2.310	9	2.315	11	2.310	21	2.315	21	2.315	58
2.227	100	2.227	21	2.227	15						

Cobalt(II) molybdate, $CoMoO_4$. Purple, and green

Source - reaction of cobalt(II) oxide with molybdenum(VI) oxide at 700° C in nitrogen.

Diffractometer traces	2θ
Sample 1 - Purple, - very poor trace	2 to 44°
Sample 2 - Purple, ground very gently -> green	2 to 44°
Sample 3 - Purple, ground more firmly -> green	2 to 44°
Sample 4 - Purple, ground very firmly -> green	12 to 35°
Sample 5 - Green, thoroughly ground sample A	2 to 44°
Sample 6 - Green, thoroughly ground sample B	2 to 35°

Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		6.76	3								
		6.33	100	6.33	93	6.28	100	6.33	100	6.33	95
						4.72	5	4.72	10		
4.69	18										
3.80	24										
						3.75	7	3.75	7	3.75	5
				3.52	11	3.51	7	3.52	9	3.52	16
3.49	21										
3.37	100	3.37	28	3.37	27	3.37	11				
3.24	27										
		3.14	81	3.14	100	3.14	77	3.14	88	3.13	100
3.10	27										
				2.771	11	2.771	10	2.763	16	2.763	27
						2.722	11				
		2.094	26	2.094	42			2.090	29		

$CoMoO_4$ (continued)

Sample 6		Reference 1		Reference 2		Reference 3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
6.33	95	6.19	70	6.27	65		
		5.51	10				
		4.72	20				
		4.44	5			4.50	100
		4.10	5				
3.75	5	3.72	20				
3.52	16	3.52	20	3.52	26	3.52	50
				3.37	14		
		3.19	5				
3.13	100	3.12	100	3.13	100	3.15	50
		2.788	5				
2.763	27	2.763	40	2.754	35		

References 1. - Smith, Acta, Cryst. 15, 1054, (1962).

2. - Ricol, Compt. Rend. 256, 3125, (1963).

3. - Forbes, Ph.D. Thesis, Edinburgh Univ. (1964).

Nickel (II) molybdate, $NiMoO_4$. Pale green

Source - reaction of nickel (II) oxide with molybdenum (VI) oxide at 700° C in air.

Diffractometer trace, 2θ = 2 to 50°.

		Reference 1		Reference 2	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
6.19	89	6.11	70	6.12	60
5.54	1	5.44	5		
4.65	2	4.65	20		
		4.40	5		
4.08	1	4.06	5		
3.71	4	3.68	20	3.80	9
3.51	6	3.49	50	3.48	30
3.16	2	3.16	5		
3.10	100	3.08	100	3.07	100
2.754	7	2.738	50	2.73	60
2.722	9	2.714	50		
2.321	2	2.321	20	2.31	20
		2.303	30		
2.186	6	2.181	30	2.19	20
2.062	45	2.058	40	2.06	50

References 1. Smith, Acta. Cryst. 15, 1054 (1962).

2. Brenner, Electrochem. Soc. 102, 7 (1955).

A.S.T.M., 9-175.

Copper (II) molybdate, $CuMoO_4$. Yellow green

Source - reaction of copper (II) oxide with molybdenum (VI) oxide at 700° C in air.

Diffractometer trace, 2θ = 2 to 45°.

Sample 1		Sample 2		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
9.31	53	9.31	26		
		7.31	10		
		6.81	8		
5.58	50	5.51	38		
4.65	62	4.65	26		
3.97	12	3.98	8	3.87	25
3.82	5	3.80	12	3.74	25
3.72	100	3.74	100	3.67	100
3.57	5	3.59	6		
3.53	7	3.53	4		
3.37	38	3.37	36		
3.33	12	3.33	20		
3.29	8	3.30	20	3.28	100
3.21	3	3.22	4	3.24	100
3.10	25	3.10	8	3.15	25
		3.02	6	3.04	25
2.989	8	2.989	10	2.932	80

Reference - Zelikman, Zhur. neorg. Khim. 1, 2782 (1956).

APPENDIX IV

X-Ray d Spacings of the Sulphates

Manganese (II) sulphate, $MnSO_4$. White

Source - dehydration of the tetrahydrate at 500° C in air.

Diffractometer trace, 2θ = 2 to 40°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.95	18		
4.44	29	4.4	16
4.06	14	4.0	16
3.72	93	3.69	80
3.65	25		
3.49	32	3.47	30
2.714	100	2.69	100
2.629	11	2.62	16
2.515	18		
2.398	36	2.36	40

Reference - The Dow Chemical Company, A.S.T.M., 3-0810.

Cobalt (II) sulphate, $CoSO_4$. Violet

Source - dehydration of the heptahydrate at 500° C.

Powder photograph.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
		6 lines	
2.53	100	2.58	100
2.24	50	2.33	15
		2.02	8
		1.96	2
		1.89	3
		1.80	8
		1.68	4
		1.63	3
		1.58	1
1.479	50	1.50	6
		1.44	2
1.392	100	1.40	8
		1.37	1

Reference - The Dow Chemical Company, A.S.T.M., 3-0843.

Copper (II) sulphate, $CuSO_4$. White

Source - dehydration of the pentahydrate at 500° C.

Powder photograph.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.04	100	4.20	53
		3.92	3
3.44	100	3.55	53
2.58	100	2.62	100
2.39	85	2.41	40
2.28	40	2.31	9
2.07	15	2.08	5
		2.01	3
1.941	60	1.96	12
1.762	100	1.77	33

Reference - Hanawalt, Analyt. Chem. 10, 457-512 (1938).

A.S.T.M., 1-1081.

Nickel (II) sulphate, $NiSO_4$. Pale green

Source - dehydration of the heptahydrate at 500° C.

Powder photograph.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.33	80	4.30	40
3.95	70	3.92	24
3.58	90	3.58	40
3.336	80	3.33	24
		3.15	2
2.567	100	2.55	100
2.334	90	2.33	40
1.999	70	2.00	20
1.957	60	1.96	6
1.866	40	1.87	10

Reference - The Dow Chemical Company, A.S.T.M., 1-1102.

APPENDIX V

X-Ray d Spacings of the Tungstates

Chromium (III) tungstate, Cr_2WO_6. Brown

Source - reaction of chromium (III) oxide with tungsten (VI) oxide at 1,000° C in air.

Diffractometer trace, 2θ = 2 to 40°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.46	58	4.43	51
4.10	42	4.05	49
3.24	79	3.22	100
2.621	18	2.614	19
2.488	100	2.481	90
2.293	12	2.285	16
2.222	5	2.217	6
2.186	9	2.181	9
2.036	6	2.036	7
1.998	9	1.994	14

Reference - Bayer, J. Amer. Ceram. Soc. 43, 495 (1960).

The Chromium (III) oxide - tungsten (VI) oxide system at 1,000° C. Diffractometer traces, 2θ = 21 to 38°.

Cr_2O_3		2:1		1:1		1:2		WO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
		4.10	35	4.10	42	4.10	38		
						3.87	58	3.85	81
						3.78	45	3.78	64
						3.68	100	3.66	100
3.65	61	3.65	8						
		3.24	73	3.24	79	3.25	70		
						3.13	5	3.13	4
						3.10	7	3.09	14
						2.706	8	2.698	14
2.683	100	2.683	11						
						2.675	9	2.675	26
						2.629	28	2.629	36
		2.621	16	2.621	18				
2.488	52	2.488	100	2.488	100	2.488	75		

Manganese (II) tungstate, $MnWO_4$. Grey

Source - reaction of manganese (II) oxide with tungsten (VI) oxide at 1,000° C under vacuum.

Diffractometer trace, 2θ = 2 to 40°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
5.79	42	5.76	22
4.85	100	4.84	63
3.78	51	3.78	59
3.72	86	3.70	56
3.01	83	2.996	100
2.960	90	2.954	95
2.885	81	2.880	29
2.502	43	2.497	54
2.481	13	2.474	9
2.417	41	2.416	19

Reference - Swanson, Natl. Bur. Stds. (U.S.), Monograph 25, sect. 2, 46 (1963).

Cobalt (II) tungstate, $CoWO_4$. Blue

Source - reaction of cobalt (II) oxide with tungsten (VI) oxide at 1,000° C in nitrogen.

Diffractometer trace, 2θ = 2 to 55°, and photograph.

		Photo.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
5.72	54				
4.69	100	4.60	25	4.67	S
				4.11	WWW
				3.98	WWW
3.75	31			3.724	S
3.63	90	3.57	40	3.608	S
				3.207	S
				3.121	WW
2.931	100	2.90	75	2.904	SSS
2.858	83	2.832	50	2.828	S
				2.723	WW
2.475	24	2.453	10	2.459	S
2.436	14	2.413	10	2.416	WW
2.338	26	2.322	40	2.332	M
2.186	17	2.169	25	2.175	S
2.045	10			2.034	W
1.986	7	1.967	10	1.976	W
				1.934	W⁻
1.903	10	1.880	5	1.8914	WW

(Over)

$CoWO_4$ (continued)

		Photo.		Reference	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
1.870	7			1.8640	M
1.807	14	1.794	75	1.7998	M
1.759	31	1.748	100	1.7521	SS
				1.7270	WW
1.698	21	1.689	100	1.6923	SSS

Reference - Broch, Skr. Norske Videnskaps Akad. Oslo, Mat. Nat. Klasse, 3, 53 (1929).

Nickel (II) tungstate, $NiWO_4$. Brown

Source - reaction of nickel (II) oxide with tungsten (VI) oxide at 1,000° C in air.

Diffractometer trace, 2θ = 2 to 41°.

		Reference		WO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
5.72	24	5.67	7		
4.65	100	4.60	32		
3.87	4			3.85	81
3.72	28	3.71	34	3.78	64
3.66	5			3.66	100
3.59	95	3.57	34		
2.894	70	2.889	100		
2.841	41	2.834	15		
2.455	20	2.455	39		
2.417	11	2.412	7		
2.303	32	2.301	12		
2.166	12	2.166	25		
2.136	4	2.131	2		
2.027	7	2.024	11		

Reference - Swanson, Natl. Bur. Stds. (U.S.), Monograph 25, sect. 2, 27 (1963).

The nickel (II) oxide - tungsten (VI) oxide system at 1,000° C in air.

Diffractometer traces, 2θ = 22 to 41°.

NiO		3:2		1:1		2:3		WO_3	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
				3.87	4	3.87	59	3.85	81
						3.78	39	3.78	64
		3.72	21	3.72	28	3.72	41		
				3.66	5	3.68	54	3.66	100
		3.59	100	3.59	95	3.59	74		
						3.36	6	3.36	8
						3.13	8	3.13	4
						3.10	9	3.09	14
		2.903	81	2.894	70	2.903	100		
		2.841	35	2.841	41	2.849	26		
						2.706	11	2.698	14
						2.675	11	2.675	26
						2.637	18	2.629	36
		2.461	20	2.455	20	2.468	26		
2.417	58	2.417	32	2.417	11	2.423	13		
		2.310	28	2.303	32	2.310	33		
		2.171	14	2.166	12	2.171	22	2.156	12
		2.136	3	2.136	4				
2.094	100	2.094	30						
		2.027	4	2.027	7				

Copper (II) tungstate, $CuWO_4$. Orange-yellow

Source - reaction of copper (II) oxide with tungsten (VI) oxide at 850° C in air.

Diffractometer trace, 2θ = 2 to 42°.

Sample 1		Sample 2	
dÅ	I/I_o	dÅ	I/I_o
5.83	65	5.87	88
4.69	100	4.69	58
3.88	32	3.90	31
3.78	10	3.78	15
3.69	9	3.71	19
3.44	76	3.44	100
3.12	23	3.12	41
2.969	15	2.979	27
2.903	66	2.912	92
2.832	18	2.841	46
2.788	12	2.797	25
2.614	6	2.614	12
2.522	7	2.522	21
2.468	6	2.468	19
2.442	4	2.442	8
2.338	30	2.338	16
2.260	2	2.265	5
2.196	2	2.196	5

APPENDIX VI

X-Ray d Spacings of the Uranates

Cobalt (II) uranate, $CoUO_4$. Black

Source - reaction of cobalt (II) oxide with uranium (VI) oxide at 1,000° C in oxygen.

Diffractometer trace, 2θ = 2 to 45°.

		Reference	
dÅ	I/I_o	dÅ	I/I_o
4.74	5	4.76	WW
4.62	61	4.61	MS
3.48	7	3.49	MW
3.25	100	3.26	S
2.780	43	2.78	S
2.675	6	2.69	W
2.374	14	2.38	M
2.298	15	2.30	MW
2.058	13	2.06	MW

Reference - Brisi, Atti Accad. Sci. Torino 95, 537 (1960).

The cobalt (II) oxide - uranium (VI) oxide system at 1,000° C in oxygen.

Diffractometer traces, 2θ = 20 to 45°.

U_3O_8		45% CoO		50% CoO		60% CoO		CoO	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
4.17	100	4.17	32						
		3.49	22	3.48	7	3.49	19		
3.43	41	3.44	28						
3.36	24	3.37	15						
		3.26	100	3.25	100	3.26	100		
		2.780	91	2.780	43	2.780	86		
		2.690	10	2.675	6	2.690	11		
2.644	38	2.644	18						
2.614	24	2.621	14						
						2.442	6	2.461	86
		2.380	27	2.374	14	2.380	26		
		2.303	16	2.298	15	2.303	16		
						2.161	2	2.131	100
2.083	24	2.076	11						
		2.062	16	2.058	13	2.058	17		

Nickel (II) uranate, $NiUO_4$. Chocolate-brown

Source - reaction of nickel (II) oxide with uranium (VI) oxide at 1,000° C in oxygen.

Diffractometer trace, 2θ = 2 to 46°.

Sample 1		Sample 2		U_3O_8	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
6.86	3	6.86	2		
5.07	6	5.07	5		
4.72	15	4.72	11		
4.35	3	4.33	3		
4.17	16			4.17	100
4.06	100	4.04	100		
3.68	10	3.68	9		
3.43	9			3.43	41
3.36	6			3.36	24
3.27	94	3.26	51		
2.960	5	2.941	3		
				2.644	38
2.629	6	2.621	2		
				2.614	24
2.556	30	2.549	20		
2.535	32	2.529	23		
2.488	3	2.481	2		
2.411	2	2.411	3		
2.327	1	2.362	1		
2.293	1	2.293	1		
2.201	2	2.196	1		
2.108	3	2.108	4		
2.083	11	2.087	7	2.083	24
2.023	19	2.018	25		

Nickel (II) uranate heated at 1,000° C in air for 2 hours.
Diffractometer trace, 2θ = 20 to 45°.

		U_3O_8		NiO	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
4.17	100	4.17	100		
3.41	54	3.43	41		
3.36	35	3.36	24		
2.644	36	2.644	38		
2.614	27	2.614	24		
2.417	5			2.417	58
2.206	1	2.217	1		
2.090	5			2.094	100
2.076	20	2.083	24		

Copper (II) uranate, $CuUO_4$. Brown

Source - reaction of copper (II) oxide with uranium (VI) oxide at 1,000° C in oxygen.

Diffractometer trace, 2θ = 13 to 41°.

		Reference		U_3O_8	
dÅ	I/I_o	dÅ	I/I_o	dÅ	I/I_o
5.10	36	5.09	50		
4.15	16			4.17	100
3.75	38	3.77	50		
3.45	100	3.45	100	3.43	41
3.29	11			3.36	24
3.26	12				
3.03	9	3.03	12		
2.876	33	2.87	35		
2.722	47	2.71	60	2.644	38
2.571	5			2.614	24
2.542	21	2.54	20		
2.481	15	2.48	20		
2.398	29	2.40	30		
2.233	9	2.23	12		